PB86-158607

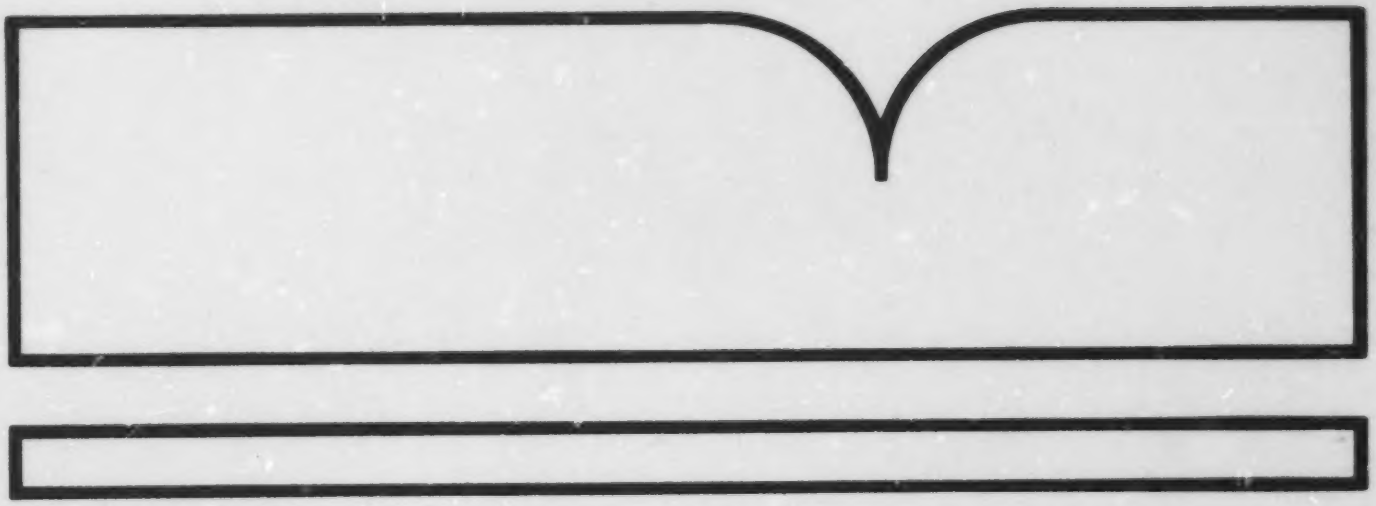
Arsenic (3) Oxidation and Removal from Drinking Water

Houston Univ., TX

Prepared for

Environmental Protection Agency, Cincinnati, OH

Feb 86



U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-158607

EPA/600/2-86/021
February 1986

ARSENIC(III) OXIDATION AND REMOVAL FROM DRINKING WATER

by

Phyllis Frank and Dennis Clifford
University of Houston
Houston, Texas 77004

Cooperative Research Agreement No. CR-807939

Project Officer

Thomas J. Sorg
Drinking Water Research Division
Water Engineering Research Laboratory
Cincinnati, Ohio 45268

WATER ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/2-86/021		PB86 158607/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
Arsenic (III) Oxidation and Removal from Drinking Water	February 1986
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Phyllis Frank Dennis Clifford	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Dept. of Civil Engineering University of Houston, 4800 Calhoun Houston, TX 77004	11. CONTRACT/GRANT NO. CR807939

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Water Engineering Research Laboratory - Cincinnati, OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Thomas J. Sorg, Project Officer 513-569-7370

16. ABSTRACT The oxidative pretreatment of As(III) using chlorine and oxygen was studied following quantification of As(III) and As(V) removals by activated alumina columns. Activated alumina removed 100 ug/L As(V) from a typical groundwater at pH 6.0 much more effectively than As(III). Approximately 23,500 bed volumes of water were treated before As(V) reached the 0.05-mg/L maximum contaminant level (MCL), whereas only 300 bed volumes could be treated before As(III) reached that level.

Variables affecting the oxidation of As(III) by chlorine include the pH, chloride concentration, other ions, chloramine formation and TOC. In artificial groundwater containing 100 ug/L As(III), a 1.0 mg/L chlorine dose oxidized 95 percent of the As(III) to As(V) in less than 5 seconds. Increasing chloride concentration slowed the reaction slightly, but not significantly for water treatment. The counterion (sodium or calcium) did not appear to affect the extent of reaction in the artificial groundwater or in chloride solutions up to 0.010 M. The presence of 5 mg/L TOC substantially slowed the oxidation kinetics of 100 ug/L As(III) by 1.0 mg/L chlorine dosage. Sparging 1 hr with oxygen did not oxidize 100 ug/L As(III) in artificial groundwater, while 100 ug/L As(III) in deionized water was approximately 14 percent oxidized. Monochloramine was found to be capable of oxidizing 40 percent of the initial 100 ug/L As(III) in the pH range of 6.5 to 10.5.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	84
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	$11.95

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This research is part of a concerted research effort at the University of Houston to examine the removal of inorganic contaminants from drinking water sources. In particular, this research examines the oxidation and removal of naturally occuring arsenic concentrations in ground water.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

The concentration of arsenic in drinking water is regulated because of the known toxicity of arsenic. A survey of unit processes for water treatment and our previous research reveal that pentavalent arsenic is more effectively removed from water than trivalent arsenic. Thus, following quantification of As(III) and As(V) removals by activated alumina columns, the oxidative pretreatment of trivalent arsenic using chlorine and oxygen was studied.

Arsenic(V) at a concentration of 0.100 mg/L was much more effectively removed from a typical groundwater by activated alumina at pH 6.0 than As(III). Approximately 23,500 bed volumes (BV) could be treated before As(V) reached the 0.05 mg/L MCL whereas only 300 BV could be treated before As(III) reached the MCL.

Variables affecting the oxidation of As(III) by chlorine include the pH, chloride concentration, other ions, chloramine formation and TOC. In artificial ground water containing no ammonia or TOC with 100 ppb As(III) present initially and 1.0 mg/L chlorine dosage, the reaction reached 95 percent completion in less than our shortest possible observation time of 5 seconds. Thus with 1.0 mg/L chlorine dosage the As(III) oxidation rate was greater than 20 micrograms/L second. The extent of oxidation at 30 seconds was insensitive to pH in the range 6.5 to 9.5, with decreasing extent of reaction outside this range. Increasing chloride concentration slowed the reaction slightly, although this effect is not significant for water treatment. The counterion (sodium or calcium) did not appear to effect the extent of reaction in the artificial goundwater or in chloride solutions up to 0.010 molar. Monochloramine is capable of oxidizing 40 percent of the initial 100 ppb As(III) in the pH range 6.5 to 10.5. The presence of 5 mg/L TOC substantially slowed the oxidation kinetics of 100 ppb As(III) by 1.0 mg/L chlorine dosage. Although the reaction reached 50 percent completion in less than 30 seconds, it did not reach 80 percent completion until approximately 30 minutes.

Sparging 1 hour with oxygen did not oxidize 100 ppb As(III) in artificial ground water, while 100 ppb As(III) in DI water was approximately 14 percent oxidized. However, capped samples of As(III) in DI water and artificial ground water were completely oxidized after 61 days on the shelf with air in the head space.

This study is part of a comprehensive research effort on arsenic removal from drinking water being carried out by researchers at the University of Houston. The related work includes field studies on As(III)/As(V) removal in San Ysidro, New Mexico and As(III) removal in Hanford, California. Previous

related laboratory studies include work on the removal of As(V) by activated alumina and anion exchange resins, and development of an analytical method for arsenic speciation.

This report was submitted in fulfillment of Grant No. CR-807939 by the University of Houston under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May 1982 to May 1984, and this work was completed as of December 1984.

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ABBREVIATIONS AND SYMBOLS

BV	Bed volume; volume occupied by adsorbent in a column, or an equal volume of solution passed through the column.
C	Concentration of solute in liquid.
C_o	Initial concentration.
DPD	N'N diethyl-p-phenylene diamine oxalate, used to quench the oxidation reaction with chlorine.
EBCT	Empty bed contact time; the time required for a volume of solution equal to the bed volume of adsorbent to pass through a column.
G	Gibbs free energy.
G^o	Standard Gibbs free energy.
G_f^o	Standard Gibbs free energy of formation.
GFAA	Graphite furnace atomic adsorption.
K	Equilibrium constant.
K_a	Acidity constant; equilibrium constant for the deprotonation reaction for an acid.
MCL	Maximum contaminant limit.
meq	Milliequivalent; one-thousandth part of standard gram equivalent.
NPOCl	Non-purgeable chlorinated organics; the non-volatile fraction of the chlorinated organics formed in water upon chlorination.
pK_a	Negative logarithm of acidity constant.
THM	Trihalomethanes.
TOC	Total organic carbon; a measure of the organics present in water.

ACKNOWLEDGMENTS

We are particularly grateful to the following individuals for their important contributions to this study:

Mr. Tom Sorg, the U. S. EPA project officer, for his continuing support, guidance, and cooperation during this and related studies, and

Dr. Arup Sengupta for his interest, helpful suggestions and encouragement during the conduct of the laboratory studies and the preparation of the report.

SECTION 1

INTRODUCTION

This study on arsenic oxidation and removal from drinking water was undertaken at the University of Houston as part of a comprehensive research effort on arsenic removal from drinking water. Related field studies using the UH/EPA Mobile Drinking Water Treatment Research Facility have been carried out in San Ysidro, New Mexico and are continuing in Hanford, California. Related laboratory studies have been done on establishing the As(V) capacity of activated alumina, regenerating arsenic-spent alumina, establishing the fundamentals of As(V) uptake by ion-exchange resins, and developing an analytical method for the separation and determination of As(III) and As(V).

Arsenic is a ubiquitous, naturally occurring, semi-metallic element. The global average concentration of arsenic in the earth's crust is 1.8 ppm. Certain geologic formations are relatively rich in arsenic, whereas, other formations contain little or none of the element. Arsenic in various inorganic or organic forms may be present in the air, soil, or water. Its presence may arise from natural phenomona such as the weathering or dissolution of arsenic-bearing rocks or from human activities such as the manufacture and application of arsenical pesticides, the combustion of arsenic-bearing coal and oil, and the smelting of various ores, commonly copper- and lead-bearing ores.

Specifically, arsenic may enter surface waters such as rivers, lakes, and estuaries in runoff from agricultural fields treated with arsenical pesticides, in various industrial wastes, and in runoff from natural rock formations that contain arsenic. Similarly, arsenic may enter ground water by a variety of routes. Inorganic arsenic may enter the ground water naturally from the dissolution of arsenic-bearing geologic formations within a given aquifer. Ground waters may also be contaminated by leachate from improperly landfilled fly ash from copper and lead smelters, wastes from arsenic refining and pesticide manufacture, tailings from ore processing, and other similar activities. Concern has been expressed about future activities such as in-situ coal gasification, which may result in the leaching of various uncharacterized organic arsenicals along with other retort products [53]. However, most arsenic-bearing ground waters currently arise as a natural phenomenon.

GENERAL CHEMISTRY

Arsenic is stable in four oxidation states (+5, +3, 0, -3) at the redox potentials (Eh conditions) occurring in most aquatic systems. The pentavalent

and trivalent states of arsenic are those most commonly encountered in solution [21]. The pentavalent form appears in solution as an anion of the triprotic arsenic acid, and the trivalent form appears as arsenious acid or its anion. The dissociation of arsenic acid (pentavalent arsenic) can be written as follows:

$$H_3AsO_4 = H^+ + H_2AsO_4^- \qquad pK_a = 2.2 \qquad (1)$$

$$H_2AsO_4^- = H^+ + HAsO_4^{2-} \qquad pK_a = 6.98 \qquad (2)$$

$$HAsO_4^{2-} = H^+ + AsO_4^{3-} \qquad pK_a = 11.5 \qquad (3)$$

The dissociation of arsenious acid (trivalent arsenic) can be written as:

$$As(OH)_3 = AsO(OH)_2^- + H^+ \qquad pK_a = 9.2 \qquad (4)$$

Thus in the pH range of 6 to 8 pentavalent arsenic occurs as either a singly- or doubly-charged anion, whereastrivalent arsenic appears as the nonionic arsenious acid. Since these species are interconvertable, arsenate should predominate in surface waters, and arsenite should be the predominant species in anaerobic ground waters. Ferguson and Gavis [21] reported that the rate of oxidation of arsenite by oyxgen is very slow at natural pH values.

OCCURRENCE

The natural occurrence of arsenic in ground water is worldwide. Various areas of the world must use arsenic-bearing ground waters as a drinking water supply. Antofagasta, Chile [5], Nova Scotia [25], and certain regions of Taiwan are three well-known examples. Various areas of the United States, most notably the southwest and the northwest regions, have a significant number of arsenic-bearing groundwaters, some of which are used as drinking water supplies [12].

Arsenic concentrations found in groundwaters vary. Examples from well-known problem areas are 0.75 mg/L total As in Antofagasta, Chile, 0.85 mg/L and 1.1 mg/L total As in Taiwan, and 0.63 and 8.0 mg/L total As in Nova Scotia [33]. In an AWWA survey of inorganic contaminants, the total arsenic concentration ranged from 0.052 to 0.19 mg/L among reported wells that exceeded the maximum contaminant limit (MCL) in use for potable water in the United States [12]. The modal concentration occurred in the 0.075 to 0.100 mg/L concentration bracket. The total arsenic concentration found in surface waters such as lakes and rivers can often exceed the concentration found in ground water. The highest values, often greater than 3 mg/L, are usually associated with human activity [17]. Naturally contaminated arsenic-bearing ground waters usually have high pH and high bicarbonate [17]. This phenomenon presumably is a result of the chemical characteristics of the arsenic-bearing rock in the aquifer.

The valence state of arsenic in ground water varies with location; however, data on the speciation of arsenic-bearing ground water is relatively scarce. A survey of various arsenic containing wells around the world

indicated that the arsenite to arsenate ratio varied from 0.007 to 1.3 [33]. These values correspond to 0.7 percent and 56.5 percent of the total arsenic in the +3 oxidation state. Drinking water wells sampled in Hanford, California, in February 1984 had a range of total arsenic concentration of 30 to 90 ppb, all of which (> 95 percent) was trivalent arsenic [16]. These well waters also contained sulfides, indicating reducing conditions within the aquifer. Ground water drawn from an infiltration gallery 4 m (13 ft) deep in San Ysidro, New Mexico contained 80 ppb total arsenic, of which 40 percent was trivalent arsenic [16]. Well water from a 13-m (43-ft) depth in this same area had a much higher total arsenic concentration (190 ppb), which was primarily trivalent arsenic. This water also contained other reduced species, namely sulfide, Fe(II), and Mn(II). From the above reports, it is apparent that both As(III) and As(V) are important species in arsenic-contaminated ground water supplies.

In a survey of individual wells at homes in Nova Scotia, Subramanian et al. [64] reported that 36 out of 50 samples exceeded 50 ppb total arsenic. Calculations made from their reported data show that 22 percent of the samples had no detectable As(III). The arsenic(III) in the remainder of the samples ranged from 0.8 to 91 percent. Nine of these samples contained As(III) in concentrations exceeding 50 ppb. In fact, six of the samples had As(III) concentrations greater than 100 ppb, with three samples exceeding 300 ppb As(III).

TOXICITY

The toxicity of arsenic is widely known. Arsenic poisoning may be acute or chronic. Both cases have been fairly well studied--the former because of the popularity of arsenic as a poison, and the latter because arsenic was the principle ingredient in Fowler's solution used to treat skin disorders and a common ingredient in various general health tonics. Ingestion of a large dosage of arsenic results in severe capillary damage that may ultimately lead to circulatory failure and death. The symptoms of chronic arsenic poisoning include diarrhea, skin pigmentation, hyperkeratosis, circumscribed edema, nausea and loss of appetite. Arsenic exerts its effect by reacting with cellular sulfhydryl groups. Thus the sulfhydryl enzymes (especially pyruvate oxidase) essential to cellular metabolism are inhibited [31].

The toxicity of arsenic depends on its valence state. Arsenite reportedly is 60 times more toxic than arsenate, primarily because arsenite inactivates the sulfhydryl enzymes. Arsenate exhibits toxicity when it is reduced to arsenite by the body [31]. Plants and animals detoxify arsenate by methylation [47]; and one bacterial species is capable of detoxifying arsenite by oxididation to arsenate. Bacteria are known to be capable of arsenate efflux through the phosphate transport system in the presence of phosphate [55, 73]. Enhanced penetration of the cellular membrane by the non-ionic trivalent arsenic may contribute to its greater toxicity, but this effect has not been measured. Increased toxicity because of penetration by non-ionized HOCl and NH_3 are, however, well known, possibly similar examples.

In addition to the toxic effects, it has also been claimed that arsenic is

a carcinogen. However, this claim is highly controversial. Epidemiological studies of increased lung cancers attributed to arsenic exposure among smelter workers in Tacoma, Washington, have been criticized on the grounds that exposure to SO_2 and other agents were not excluded [19]. The increased incidence of skin cancers attributed to arsenic ingestion in drinking water in Taiwan has also been questioned because that water also contained ergometrine and other fluorescent alkaloids that cannot be discounted as carcinogens [24, 56]. Other instances of arsenic ingestion by means of drinking water have failed to produce an increased incidence of cancers [56]. Furthermore, experiments to induce cancer in laboratory animals have failed to demonstrate that arsenic acts as a carcinogen [24]. Those experiments where cancers have been induced have such low animal survival rates (< 5 percent) as to make the results meaningless [24]. Therefore, it has not been demonstrated that arsenic is a carcinogen [24, 44].

In fact, some current research indicates that arsenic may be an essential trace element. Arsenic in the form of organic arsenicals has been used as a feed additive for poultry and swine to promote weight gain [2]. Such observations have promoted research into the nutritional value of arsenic. Recent research indicates that arsenic may be an essential trace element in chickens and goats [44, 69] with a relationship between zinc and arsenic metabolism. However, the metabolic studies seem to deal only with the +5 oxidation state. Although the toxcity of arsenic is well-known, its exact role and influence in human metabolism remains unknown-- and fraught with controversy.

Despite the lack of knowledge about the consequences of the ingestion of very small amounts of arsenic, the ultimate toxicity of arsenic is well recognized. It is for this reason that the concentration of arsenic in foodstuffs and water is regulated. The USEPA National Interim Primary Drinking Water Regulations set a Maximun Contaminant Limit (MCL) for arsenic at 0.05 mg/L.

ARSENIC REMOVAL

Trace amounts of arsenic are usually successfully removed by conventional water treatment methods [46]. For a number of surface water sources with significant levels of arsenic, arsenic occurrence in the finished water was relatively infrequent after conventional water treatment [43]. Experimental studies have shown that arsenic may be removed by coagulation, filtration, reverse osmosis, ion-exchange, electrodialysis, and adsorption onto activated alumina. In most of these processes it is pentavalent arsenic that is removed most effectively. Only the removal of inorganic arsenic will be discussed here because organic species such as monosodium methyl arsenic (MSMA) do not appear to be a problem in ground water used for potable water supply.

Removal by Coagulation

In the environment, arsenic can be removed from solution by coprecipitation with metal ion precipitation, most notably the iron oxides [21]. In treatment plants and experimental studies, arsenic has been removed

with varying degrees of success by coagulation and precipitation, primarily with aluminum and iron hydroxides. This process is usually followed by filtration. Lime softening has also been studied for arsenic removal. Of the various coagulants, ferric chloride has proved the most successful. Arsenic removal by coagulation appears to be dependent upon initial arsenic concentration, dosage of coagulant, pH, and the valence of the arsenic species as will be discussed below.

Alum--

In early alum precipitation experiments by Buswell [7], some removal of high initial arsenic concentrations (25 mg/L) at pH 6-7 was achieved. Rosehart and Lee [51] found alum to be moderately successful in removing high concentrations of arsenic (132 mg/L) from gold mine wastes. Addition of alum to these waters in an Al/As ratio of 4:1 at pH 7-8 achieved a maximum 90 percent removal of As(V) to a final concentration of 13.2 mg/L. The removal of lower concentrations of As(III) was successful. Under the same optimal dosage and pH conditions, 500 ppb As(III) was reduced 95 percent to 25 ppb. However, Shen [57] achieved only a 32 percent removal of 1 mg/L arsenic with 20 mg/L alum at pH 6.8. Although the valence state was unspecified, the ground water presumably contained As(III) as it also contained sulfides and ammonia, indicating reducing conditions. This observation agrees with what is known about the poor removal of As(III) by activated alumina--dehydrogenated $Al(OH)_3$.

Nillson [45] also investigated arsenic removal by alum. At an initial concentration of 21 mg/L As(V) at pH 6.5-7, a 94 percent removal was achieved with a 10 mg/L alum dosage. However, these same conditions failed to remove any of 23 mg/L As(III). Under these same conditions of pH and alum dosage, 71 percent removal of an initial concentration of 4.2 mg/L As(V) was achieved. An examination of these data indicates that As(V) is much better removed by alum than As(III). And, although data is usually presented as percent removal which tends to obscure the point, as the initial concentration of arsenic increases, the arsenic remaining after coagulation and precipitation also increases.

The extensive research by Logsdon [42] supports these trends. Alum coagulation resulted in a 5-15 percent removal of As(III) which was considerably less than the removal of As(V) Gulledge and O'Connor [27] obtained under the same conditions. Gulledge and O'Connor found that greater than 90 percent removal of arsenic(V) could be acheived with 30 mg/L dosage of alum at pH 5-7. Logsdon [60] also found that coagulation with 30 mg/L alum could achieve the arsenic MCL with arsenic(V) concentrations of 1.5 mg/L or less, but the MCL was not obtainable when the arsenic(III) concentration was 0.1 mg/L or higher unless As(III) was oxidized to As(V) prior to coagulation and precipitation.

The optimal pH and alum dosage for arsenic removal appear to be specific to each water. Despite this observation, certain general trends are followed. Pentavalent arsenic is more effectively removed than trivalent arsenic under the same optimal conditions. This result is an important consideration in

drinking water treatment when a certain MCL needs to be achieved. Also, the higher the initial concentration of arsenic, the higher the concentration remaining after alum coagulation and precipitation.

Iron--

Numerous coagulation and precipitation experiments with some form of iron, principally either ferric or ferrous sulfate, or ferric chloride, have been performed--often in conjunction with alum precipitation experiments. One study by Pierce and Moore [48] obtained very high arsenic removal rates with amorphous $Fe(OH)_3$. Ferric hydroxide at 4.45 mg/L removed 119 mg/g at 0.53 mg/L As(V) and 37.5 mg/g at 0.83 mg/L As(III). Buswell [7] observed an 84 percent removal of 25 mg/L As(V) after coagulation, precipitation, and filtration at pH 5-6 with 250 mg/L of "Ferrisul" ferric sulfate. As(III), only after oxidation to As(V) with calcium hypochlorite, was removed to 4 mg/L under the same conditions. Cherkinskii [10] reported a 96 percent removal of 36.2 mg/L arsenious oxide with a ferrous sulfate dosage of 750 mg/l. Rosehart and Lee [51] obtained 94 percent removal of 132 mg/L As(V) at pH 8 with ferrous sulfate at a Fe/As ratio of 1.5, but failed to remove any of 0.5 mg/L As(III) under these same conditions. Using ferric chloride as the coagulant at a higher Fe/As ratio of 4.0, 90 percent removal of 132 mg/L As(V) at pH 9 and 95 percent removal of 0.5 mg/L As(III) at pH 8 was obtained. With both ferrous sulfate and ferric chloride, removal of As(III) was more difficult than removal of As(V). Gulledge and O'Connor [27] demonstrated that ferric sulfate doses of 30 mg/L at pH 5-8 would remove 0.05 mg/L As(V) almost completely. Shen tested both ferrous sulfate and ferric chloride. He preferred the ferric chloride in his treatment plant design because he achieved greater removal (82 percent versus 24 percent) of 1.0 mg/L arsenic at pH 6.7 and 20 mg/L coagulant. Although the valence was not stated, arsenite is presumed to be the predominant species because the water was anaerobic and contained other reduced species. Shen also obtained 98.7 percent removal of 0.80 mg/L arsenic after 20 mg/L chlorination --indicating oxidation. Sorg and Logsdon [60] achieved high removal rates (81 percent or better) of As(V) with ferric sulfate at pH 6.7 to 8. However, As(III) was removed only at very low initial arsenic concentrations.

Pierce and Moore [48] concluded that the adsorption of arsenic onto ferric hydroxide was not solely because of electrostatic processes, but included specific adsorption or the formation of a chemical bond. Furthermore, their results showed that arsenate adsorption was 20 times faster than arsenite adsorption. They concluded that for concentrations found in natural waters the optimum pH for arsenite removal is 7 and for As(V) removal pH 4 is optimal. While other researchers, as discussed above, were able to remove both states at other pH values, As(V) was always removed more effectively then As(III). This result is important when attempting to remove arsenic to meet the MCL.

Lime softening--

Lime softening removes arsenic probably by co-precipitation of calcium arsenate on the hydrous magnesium oxide floc. Lime softening followed by

filtration removed arsenic from water in Argentina [66]. Hard, turbid waters were treated with lime and recarbonated to adjust pH. However, further details were not given in the reference.

Cherkinskii [10] studied arsenic removal by lime softening along with coagulation by ferrous sulfate. A dosage of 2250 mg/L of calcium oxide was required to remove 96 percent of 362 mg/L arsenious oxide. However, pH and the alkalinity, important variables in softening, were not given.

Various researchers have described arsenic removal by lime softening from mining waste streams. Laguitton [36] wrote that arsenic valence, pH, calcium activity and phosphate concentration are important variables for maximizing arsenic removal. Rosehart and Lee [51] attained removal of 123 mg/L As(V) to 6.6 mg/L at pH 12 with CaO. The optimal Ca/As ratio was 9.8. Under these same optimal conditions, a 95 percent removal of 0.50 mg/L As(III) to 0.025 mg/L was attained.

In his investigation on drinking water treatment, Nillson [45] was unable to remove by lime precipitation any of 23 mg/L As(III) at pH 9.5 after pretreatment of tap water with 6 mg/L phosphate as P. In tap water with 21 mg/L As(V), treatment with lime at pH 9.5 removed arsenic to 9.7 mg/L. At an arsenic concentration of 4.2 mg/L As(V) in "mechanically treated" municipal wastewater, lime treatment at pH 9.5 yielded a minimum of 0.1 mg/L for a maximum removal of 98 percent. The nature of the mechanical treatment was not specified. Shen [57] obtained only a 20 percent removal of 1.0 mg/L arsenic after a dosage of 20 mg/L lime. The pH of the raw water was 6.8, but the pH attained was not given. Also, as noted before, the valence of the arsenic was not given but was presumably As(III). Sorg and Logsdon [60] conducted pilot plant lime softening tests at pH 9.5 and 11.3, the latter tests included recarbonation and second stage settling. Lime softening at pH 9.5 resulted in 10 percent removal of 0.48 mg/L As(III) and 49 percent removal of 0.42 mg/L As(V). At pH 11.3, 63 percent removal of 0.34 mg/L As(III) was attained after first-stage treatment and 69 percent overall removal after the second-stage. At this pH, 98 percent removal of 0.58 mg/L As(V) was attained after first-stage treatment. Second-stage settling did not improve removal. Arsenic(III) removal was always poorer than arsenic (V) removal. They concluded that the arsenic MCL can be attained only if 0.35 mg/L or less As(V) is present initially, and if As(III) concentrations are less than 0.1 mg/L, preoxidation is not necessary to achieve the MCL when softening is performed at pH 10.7 or above.

None of the researchers have examined all the variables that Laguitton theorized were important in maximazing arsenic removal. However, the work to date shows that the removal of arsenic to meet an MCL depends significantly upon the valence state and the pH. Higher pH appears to increase removal and As(V) is more effectively removed than As(III).

Removal during Filtration

Much of the filtration data has been collected in conjunction with arsenic co-precipitation experiments. Shen [57] studied filtration with sand and

anthracite. At slow filtration rate (2-4 m^3/m^2 day), a sand column 48 cm long removed 90 to 95 percent of 1 mg/L arsenic, while an anthracite column 70 cm long was needed to achieve 95 percent removal. Slow sand filtration yielded better arsenic removals than rapid sand filtration (168 - 194 m^3/m^2/day); however, the filter runs proved too short to be useful for practical application. Sorg and Logsdon [60] also studied filtration after coagulation and precipitation. Increased removals were obtained by following coagulation with dual media filtration. Filtration with granular activated carbon (GAC) yielded only slightly higher removals than filtration with dual media.

Filtration studies like those above were conducted as polishing steps. The mechanism of action can be attributed at least partially to adsorption. Sand is known to absorb both As(III) and As(V) differentially [26]. Elution profiles of 0.180 mg/L As(V) and As(III) from sand columns show that As(III) elutes much faster than As(V) under oxidizing and neutral conditions, and at approximately the same time under strongly reducing conditions. This behavior is attributed to differential adsorption.

Removal by Reverse Osmosis

Preliminary studies by Fox [23] showed reverse osmosis to be effective in removing arsenite and arsenate from water. Both the DuPont (aramid) and the Osmonics (cellulose acetate) membranes removed 0.750 mg/L below the detection limit, probably 0.005 mg/L. Pentavalent arsenic was removed to meet the MCL when the initial arsenic concentration was 4 mg/L for the aramid membrane and 6 mg/L for the cellulose acetate membrane. A maximum removal of 80 percent was achieved for trivalent arsenic. Studies by Fox [22] for the EPA in Fairbanks, Alaska and Eugene, Oregon show 96 to 98.6 percent removal of 0.42 to 0.46 mg/L arsenic. The speciation of arsenic was not available. Point of use research directed by Sorg [59] at the Drinking Water Research Division EPA, studied arsenic removal by a household reverse osmosis unit. Pentavalent arsenic was generally better removed than trivalent arsenic. Removals of arsenite from well water varied from 43 percent to 81 percent while removals for arsenate were 97 to 99 percent. Chlorination of the As(III) bearing waters increased removal in two out of three cases. The removal of As(V) by reverse osmosis is more effective as expected because As(V) exists as an anion while As(III) is non-ionic in the pH range of interest, and as such more easily penetrates the membrane.

Removal by Electrodialysis

Electrodialysis (ED) is a process that would be expected to remove As(V) preferentially over As(III) since the basis of removal depends upon the existence of charged species. Since arsenate exists as an anion for pH above 2.2, while As(III) exists predominantly in its non-ionized form below pH 9.2, As(V) should be preferentially removed over As(III) below pH 9. Reversible electrodialysis (EDR) was studied for arsenic removal in New Mexico using the University of Houston/EPA Mobile Drinking Water Treatment Research facility [16]. Water from San Ysidro, NM Well No. 4 containing 190 ppb total arsenic which was predominantly As(III) was treated by EDR. Most of the arsenic (140 ppb) remained in the product indicating poor removal of As(III). However,

more research is needed in this area.

Removal by Adsorption

Adsorption by a variety of sorbents has been widely investigated because of the inherent advantages of packed beds. Two of the most commonly used adsorbents are activated carbon and activated alumina although a variety of other adsorbents have been studied and utilized in water treatment.

Gupta and Chen [28] investigated the adsorption of arsenic by activated alumina, activated bauxite, and activated carbon. These studies indicated that activated carbon was ineffective in removing arsenic from water. This conclusion was generally supported by Sorg and Logsdon [60].

On the other hand, activated alumina can successfully remove arsenic from water. Bellack [3] removed arsenic from ground water in Fallon, Nevada using activated alumina (F-1 grade Alcoa, 28 X 48 mesh) in 18.5 mm-ID glass columns filled with 25 gm at an optimum flow rate of 2.5 to 3.0 gpm/sq. ft. Initial arsenic concentration was 0.106 mg/L and the runs were terminated when the effluent arsenic concentration reached 0.01 mg/L.

The previously mentioned studies by Gupta and Chen [28] indicated that arsenic was strongly absorbed by activated alumina. At 0.300 mg/l As(V) final concentration, the equilibrium adsorption capacity was approximately constant at 7.5 mg As(V)/g alumina for various solution salinities from fresh water through 0.67 N NaCl and "$Fe(OH)_3$-precipitated" sea water. However, at a low equilibrium concentration for 0.50 mg/L As(V), the capacity varied from 1.0 mg As(V)/g alumina for sea water to 4.2 mg As(V)/g alumina for fresh water. No explanation of this observation was given. He also observed that the rate of adsorption decreased wih increasing salinity, and that the As(V) capacity of alumina was a strong function of pH.

However, these experiments by Gupta and Chen indicated that the adsorption of As(III) onto alumina was not pH dependent in the range 4 to 9. Between pH 4 and the optimum pH 9, a nearly constant 0.2 mg As(III)/g alumina was absorbed at equilibrium with fresh water. This adsorption capacity is substantially less than that for As(V).

At arsenic concentrations of about 4 mg/L As(V) and 1 mg/L As(III), silica at concentrations of 70 mg/L and higher provided significant competition. This result is what would be expected since silica, especially the ionic form, is a highly preferred ion by alumina [13].

Further investigation on arsenic adsorption onto alumina was performed by Rosenblum and Clifford [52]. They found that arsenic adsorption onto alumina was optimized at pH 6.0 in column tests with an influent concentration of 1.0 mg/L As(V) in artifical groundwater. Arsenic adsorption was found to be significantly reduced by anion competition. At a liquid-phase equilibrium concentration of 1 mg/L As(V), adsorption of arsenic was reduced by over 50 percent in the presence of 15 meq/L SO_4^{2-} and 20 percent in the presence of 15 meq/L Cl^- compared to deionized water. An As(V) adsorption capacity of

16.1 mg As(V)/g alumina at 1.0 mg As(V)/L was obtained from minicolumn tests. Column tests on As(III) adsorption resulted in much higher than expected maximun adsorption capacities. Upon examination of the arsenic effluent histories they concluded that oxidation of As(III) had occured during the run probably as a result of microbial action. Further studies on As(III) adsorption need to be conducted.

Removal by Ion Exchange

Calmon [9] investigated the use of cation and anion exchangers for the removal of 68 mg/L arsenic from "field waters". Not suprisingly, cation exchangers were ineffective; however, removals of 55 to 82 percent were obtained with various anion exchange resins in the chloride form. Removals of 99 and 100 percent were obtained in column tests. Other pertinent information was not given in the reference cited.

Shen [57] conducted a column test with the weak-base resin Ionac A-260. After 6.6 bed volumes of synthetic water containing 1 mg/L As(III), only 21 percent removal was occuring. However, well water treated in the same manner resulted in the complete removal of arsenic. These results are hard to definitively explain without feedwater pH data, arsenic speciation in the well water, and the concentrations of competing anions such as sulfate in both test waters. However, at acidic pH which weak-base resins require in order to act as ion exchangers, As(III) is non-ionic and would not be expected to be significantly removed. The well water which presumably contained at least some As(III) because of the presence of other reduced species may have been oxidized upon standing prior to ion exchange treatment.

Lee and Rosehart [72] investigated several ion-exchange resins. They obtained removal of arsenic with various resins; however, lack of information on the arsenic speciation and the presence of other ions severely limits the usefulness of their results.

Horng and Clifford [32] studied the removal of arsenate by strong-base ion exchange. A study of five anion-exchange resins (Amberlite IRA-900, Ionac ASB-1, Ionac ASB-2, Dowex 11, Amberlite IRA-458) resulted in the conclusion that Amberlite IRA-458, an acrylic-amine, microporous resin with quaternary fuctionality, was the most arsenate selective resin tested. All of the strong-base anion exchange resins tested at arsenate and carbonate concentrations likely to be encountered in ground water gave the following anion selectivity sequence:

$$SO_4^{2-} > HAsO_4^{2-},\ CO_3^{2-} > Cl^- > H_2AsO_4^-,\ HCO_3^-$$

However, because arsenate is less preferred than sulfate, chromatographic elution of arsenic occurred. This chromatographic peak phenomena will occur for all species less preferred than the most preferred species present. This effect is one very serious drawback to the use of strong-base ion-exchange for the removal of arsenate.

Studies on strong-base ion-exchange resins indicate that As(III) is not

removed at neutral and acidic pH. In fact, Amberlite IRA-458 was used to separate As(III) from As(V) by Clifford et al.[15]. Weak-base ion exchange resins, which must operate at acidic pH, also do not remove As(III). It is not suprising that ion exchange is ineffective for the removal of trivalent arsenic as it exists predominantly as the non-ionized arsenious acid (pK_1 = 9.22) at the pH values exchangers are operated. For this reason, while ion exchange can remove pentavalent arsenic in the pH range of interest (6-9), trivalent arsenic is removed ineffectively if it is removed at all.

SUMMMARY

In the treatment processes discussed, pentavalent arsenic is, without exception, more effectively removed from water than trivalent arsenic. Thus oxidative pretreatment of trivalent arsenic will improve the arsenic removal from waters containing As(III).

SECTION 2

CONCLUSIONS

Arsenic(V) is much more effectively removed by activated alumina than trivalent arsenic. An Alcoa F-1 activated alumina column operated at pH 6.0 removed 18 g As(III)/ m^3 alumina, whereas 1610 g As(V)/m^3 alumina was removed when the effluent concentration of arsenic reached 0.05 mg/L.

The oxidation of ppb levels of arsenic(III) by ppm levels of chlorine is very rapid in aqueous solution. The oxidation of 100 ppb of As(III) by 1.0 mg/L free chlorine in artificial ground water reached completion (95 percent) within 5 seconds. Thus for water treatment purposes, contact times do not need to be particularly long. The extent of oxidation of 100 ppb As(III) by 1.0 mg/L free chlorine in artificial ground water was insensitive to pH after 30 seconds of reaction time in the range of 6.5 to 9.5. The oxidation of 100 ppb As(III) by 1.0 mg/L free chlorine reached 90 percent completion in the presence of 0.01 M chloride. The counterion (sodium or calcium) had no significant effect on either the kinetics or extent of oxidation. For most groundwaters, oxidative pretreatment with free chlorine may be effective in enhancing arsenic removal.

In artificial ground water, 100 ppb As(III) was oxidized by 1.0 mg/L monochloramine in the presence of excess ammonia. Only a third of the As(III) was oxidized, however. This reaction was also insensitive to pH in the range 6.5 to 10.5. Although oxidation by monochloramine can occur, the As(III) remaining may exceed the MCL.

Arsenic(III) oxidation by 1.0 mg/L chlorine in aged tap water (TOC = 5 mg/L) was considerably slowed. The reaction did not reach 95 percent completion until 60 minutes. The extent of reaction was the same as that for oxidation in artificial ground water. Presumably, oxidation was slowed by the chlorine demand of the TOC present in the water. Chlorine contact times that are sufficient will be important for efficient water treatment.

Although very slow, oxygen is capable of arsenic oxidation. Sparging for 60 minutes with oxygen oxidized only 3 percent of 100 ppb As(III) in artificial ground water, but 14 percent of 100 ppb As(III) in DI water was oxidized. However, samples of As(III) in DI water and artificial ground water were completely oxidized after 61 days of sitting in bottles with air in the head space.

SECTION 3

RECOMMENDATIONS

LAB STUDIES

Further studies will prove useful for producing optimum arsenic(III) oxidation by chloramine for subsequent arsenic removal. The limitations of this treatment need to be examined experimentally. The extent of As(III) oxidation by monochloramine may vary with the monochloramine concentration and the amount of excess ammonia present. Experiments under the conditions used in this work with different monochloramine dosages (i.e. 0.5, 2.0, 5.0, 10.0 mg/L) and different amounts of excess ammonia should help determine whether free chlorine or combined chlorine is the actual oxidant. Also, further study of longer reaction times may indicate which is the true oxidant.

PILOT STUDIES

Pilot studies of arsenic(III) oxidation by chlorination of actual arsenic-contaminated waters may be beneficial. The presence of reduced species such as sulfides, Fe(II), and Mn(II) may adversely affect the ease of arsenic(III) oxidation. Furthermore, species such as copper are known to catalyze the destruction of HOCl, which may adversely affect the extent of reaction at a given chlorine dosage. Although laboratory studies look promising, it may be difficult to obtain good oxidation in the field at the low chlorine dosages such as are required for electrodialysis and reverse osmosis membranes.

Further investigation of whether mechanical aeration or ponding can provide adequate oxidation for subsequent arsenic removal may also be useful. The advantage of these methods is that they are relatively low cost and require little maintenance.

SECTION 4

THEORY

AQUEOUS ARSENIC CHEMISTRY

Arsenic occurs in the +3, +5, 0, and -3 oxidation states; however, under the pH and Eh (redox potential) conditions found in natural waters, only the +3 and +5 states are stable [21]. In aqueous systems, pentavalent arsenic occurs as arsenic acid or its anions. Trivalent arsenic may occur as arsenious acid, its anion, or arsenious anhydride. The latter species is an amphoteric soluble solid. Figure 1 shows the influence of pH on the solubility of As_2O_3 in aqueous solutions. However, as shown is Figure 1, at the concentrations generally encountered in natural ground waters, arsenious anhydride dissolves completely with the formation of primarily undissociated arsenious acid--H_3AsO_3. Thus, at the concentrations of interest, trivalent inorganic aqueous arsenic occurs as arsenious acid or its anion.

Arsenic acid, H_3AsO_4, is a triprotic acid with $pK_1 = 2.2$, $pK_2 = 6.98$, and $pK_3 = 11.5$, and appears in solution as either the acid or the corresponding anion. Monoprotic arsenious acid (pK = 9.2) may be written as $HAsO_2$. However, strong evidence suggests that $HAsO_2$ and its anion do not actually appear in solution [58]. Arsenious acid appears to be $As(OH)_3$ with the following three possible anionic species depending upon the basicity of the solution: $AsO(OH)_2^-$, $AsO_2(OH)^{2-}$, and AsO_3^{3-}. However, the only disocciation that occurs in the range of interest is:

$$As(OH)_3 = H^+ + AsO(OH)_2^- \qquad pK = 9.2 \qquad (1)$$

Arsenic is not known to form ligands with water; the species $As(H_2O)_m^{n+}$ is probably not formed. Although As(III)-Cl bonds are known to occur, these bonds only occur at high HCl concentrations [58]. Disproportionation reactions are not known to occur with either of the acids. Thus the arsenic oxyions are the principle species of environmental interest.

Figure 2 shows the regions of thermodynamic stability of the relavent trivalent and pentavalent arsenic species at various pH and Eh values. The equations used to construct the diagram after the method of Stumm and Morgan [63] are presented in Appendix 1. As Figure 2 shows, three different arsenic oxidation half reactions are possible in the pH range 4 to 11. Thus the oxidation potential of arsenic half reactions is a function of pH. Figure 2 also shows that under aerobic conditions, pentavalent arsenic is the thermodynamically stable species. Therefore, oxygen is capable, at least theoretically, of oxidizing As(III) to As(V).

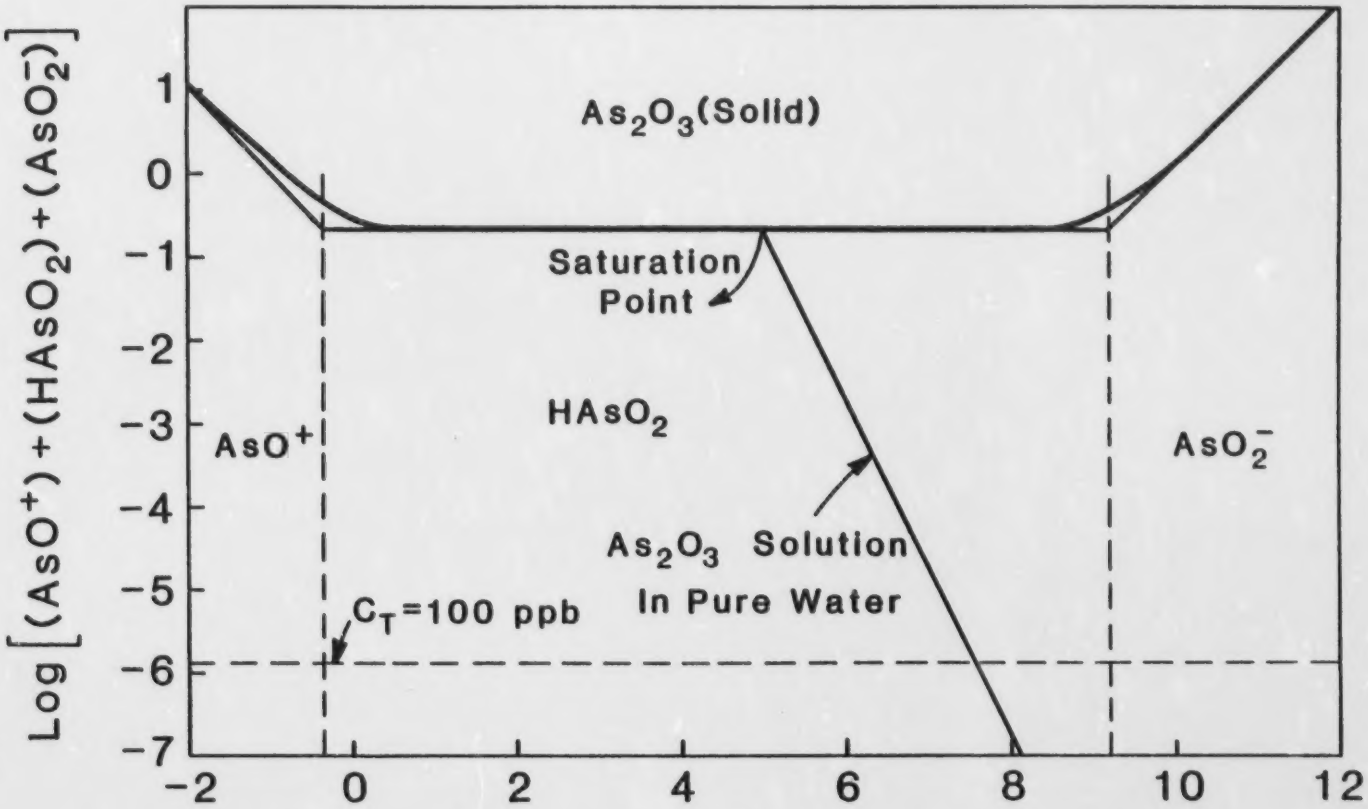

Figure 1. The influence of pH on the solubility of arsenious anhydride.

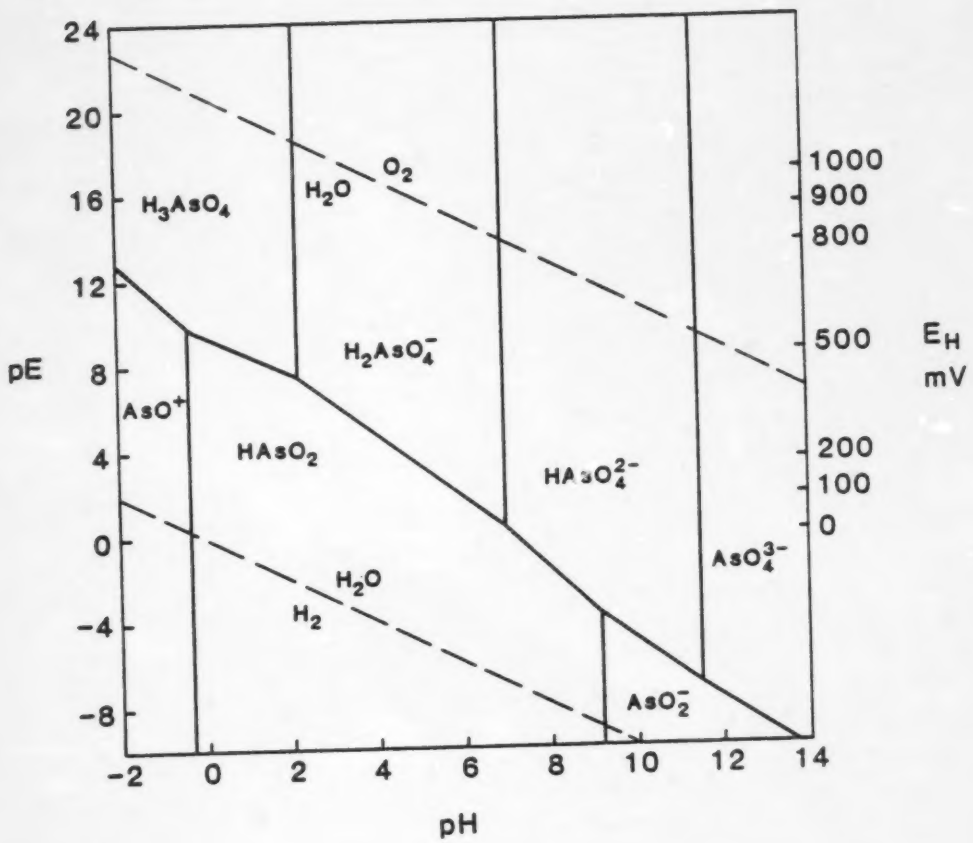

Figure 2. pE - pH diagram for arsenic-water system at 25°C.

OXIDATION STUDIES

Pourbaix [49] reported that the oxidation of arsenic(III) occured only under conditions of considerable overpotential. Oxidizing agents listed were the halogens or their oxygen compounds, chromic acid, nitric acid, hydrogen peroxide, or permanganate. Johnson and Bruckenstein [35] studied As(III) oxidation by I_2 at pH 8.2 to 9.2 and discovered the rate expression to be:

$$\frac{-d\ As(III)}{dt} = k[I_3^-][H_2AsO_3^-] + k_1[I_2]\ [H_2AsO_3^-] \qquad (2)$$

$$= k_{obsd}[I_3^-][As(III)]$$

where $[As(III)] = [H_3AsO_3] + [H_2AsO_3^-]$.

Roebuck [58] reported the rate of oxidation in acidic media to be

$$\frac{d\ As(III)}{dt} = \frac{k_f[As(III)][I_3^-]}{[I]^2\ [H^+]}$$

$$= k_{obsd}[As(III)][I_3^-]$$

Liebhafsky has proposed a mechanism to explain this behavior. Studies on As(III) oxidation by bromine showed the reaction to be zero order in bromine [58]. Other studies on oxidation of As(III) in strong HCl solutions demonstrated that the kinetics showed a complicated dependence upon HCl [58].

Chlorine has been used as an oxidant by Shen [57], Sorg and Logsdon [60], and other researchers in drinking water treatment; however, studies of kinetics or the effects of pH and ions in solution have not been reported. And although As(V) is the thermodynamically stable species under aerobic conditions, the oxidation of As(III) by oxygen is reported to occur very slowly at neutral pH [21].

AQUEOUS CHLORINE CHEMISTRY

Chlorine is a common disinfectant and oxidizing agent for water treatment. Consequently, the aqueous chemistry of chlorine has been extensively studied and reviewed. The various chlorine species can participate in the following types of reactions: hydrolysis, redox, chloramination, substitution, addition, atom exchange, radical oxidation, photochemical decay, metal catalyst decomposition, and self decomposition. All of these reactions can occur under natural water conditions. However, only the environmentally significant reactions will be considered for simplicity.

Figure 3 shows the regions of thermodynamic stability of the most significant chlorine species. The equations used to construct the figure are given in Appendix 2. As Figure 3 shows, chloride is the stable species in water under all conditions. A comparison of Figures 2 and 3 indicates that considerable overpotential exists for the oxidation of As(III). At a typical

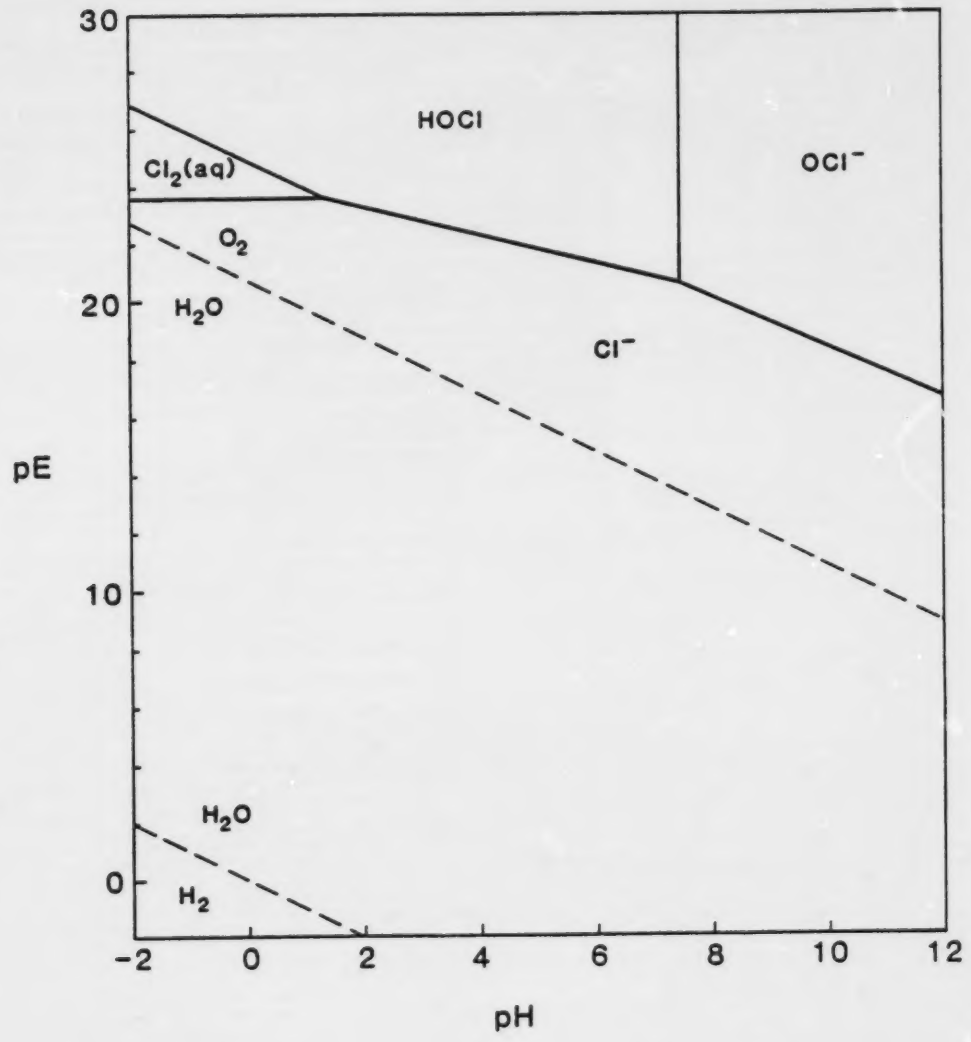

Figure 3. The pE - pH diagram for chlorine in water, 25°C.

ground water pH of 8.0, the border of thermodynamic stability for As(III) occurs at Eh = -100 volts while the border of thermodynamic stability for the chlorine species OCl^- occurs at Eh = 1200 volts.

Free Chlorine

Chlorine gas dissolves instaneously in water by rapid and reversible hydrolysis.

$$H_2O + Cl_2 = HOCl + H^+ + Cl^- \quad (4)$$

Increasing H^+ or Cl^- can cause Cl_2 to predominate at equilibrium thereby decreasing hypochlorous acid (HOCl) formation. This behavior is found to occur in sea water [29].

Hypochlorous acid is a weak acid which dissociates as follows:

$$HOCl = H^+ + OCl^- \qquad pK = 7.5 \quad (5)$$

At pH < 7.5, HOCl is the dominant species while at pH > 7.5 OCl^- is the dominant species. Each of these species has a different redox potential. Free chlorine species (HOCl, OCl^-, Cl_2, H_2OCl^+, Cl^+) are capable of oxidizing I^- and Br^- to HOI and HOBr resulting in the formation of brominated and iodinated trihalomethanes (THM) in chlorinated natural waters. Since chlorine species are so reactive, other constituents of natural water such as ammonia and organics effect the performance of chlorine as an oxidizing agent for a target species.

Combined Chlorine

The term "combined chlorine" refers to the halogenated nitrogen compounds such as monochloroamine, dichloroamine, trichloroamine, and organic haloamine. The formation of chloroamines from ammonia occurs in a stepwise manner:

$$HOCl + NH_3 = NH_2Cl + H_2O \qquad \text{fast} \quad (6)$$

$$HOCl + NH_2Cl = NHCL_2 + H_2O \qquad \text{slow} \quad (7)$$

$$HOCl + NHCl_2 = NCl_3 + H_2O \qquad \text{slow} \quad (8)$$

The chloramines obtained depend upon pH, reaction time, the relative concentration of HOCl and NH_4^+, and temperature [18]. At pH greater than 8 and a molar ratio of HOCl to NH_4-N of 1:1 or less, monochloramine is observed. Usually nitrogen trichloride is the only species detected at pH less than three [18, 29]. Under certain conditions, the formation of chloramines is reversible; however, the equilibrium state probably is rarely attained because the reverse reaction is so slow in comparison to the forward reaction. The mono- and dichloramines retain some disinfecting power, although much less than an equivalent concentration of free chlorine. Free chlorine reacts with organic amines to form the organic haloamines RNHCl, $RNCl_2$, R_2NCl, but not

much is known about the mechanisms of these reactions.

Chlorine Oxidant Decay

Hall [29] describes chlorine oxidant decay as any reaction involving conversion of chlorine into constituents that are not detectable by the analytical methods for free chlorine. Decay reactions are summarized in Appendix 3; however, only those reactions with significance to this research will be discussed.

The formation of total organic halogen compounds (TOX) that can be further hydrolyzed to yield non-haloform and THM is perhaps the most important chlorine decay reaction [43]. Fleischaker and Randtke [20] report that the substitution and addition reactions to form non-purgable chlorinated organics (NPOCl) are faster than the oxidation of organic matter by chlorine and perhaps faster than the hydrolysis of chlorinated intermediate byproducts to form chloromethanes.

Another important set of reactions are those associated with the oxidation of ammonia-nitrogen and the phenomenon of breakpoint for residual chlorine. When the molar ratio of chlorine to nitrogen exceeds 1:1, the unstable species $NHCl_2$ is formed which subsequently decays to N_2 and NO_3^- resulting in a loss of ammonia-nitrogen. However, if the molar ratio exceeds 1.5, NCl_3 is formed resulting in a preservation of ammonia-nitrogen [18, 29]. These reactions occur during chloramination prior to the breakpoint where free chlorine begins to exist.

Other reactions of lesser importance in oxidant decay in water treatment are the oxidation of inorganic ions and the self-decomposition reactions. Lister [39] reported that Fe(II) and Mn(II) were oxidized by OCl^- with no catalytic activity. Other inorganic ions are susceptible to attack; these ions include nitrite, sulfite, selenite and arsenite. Nickel, cobalt, and copper ions catalyze the decomposition of OCl^- to O_2 and Cl^-. Mechanisms of inorganic ion oxidation will be discussed later. Under certain conditions the self-decomposition of OCl^- and HOCl to form O_2, ClO_2, ClO_3^-, ClO_2^- and Cl^- occurs [29].

REACTION THERMODYNAMICS

A study of thermodynamics shows whether a reaction is possible and how potentially energetic it is. Since the pK values of hypochlorous acid, arsenious acid, and arsenic acid are known, four reactions are possible depending upon the pH. The following half reaction potentials are from the thermodynamic data of Latimer [37], Sillen [54], and Pourbaix [49].

$$HOCl + H^+ + 2\ e^- = Cl^- + H_2O \qquad (9)$$

$$E = 1.49 \text{ volts}$$

$$OCl^- + H_2O + 2\ e^- = Cl^- + 2\ OH^- \qquad (10)$$

$$E = 0.90 \text{ volts}$$

$$HAsO_2 + 2\ H_2O = H_2AsO_4^- + 3\ H^+ + 2\ e^- \quad (11)$$

$$E = 0.666 \text{ volts}$$

$$HAsO_2 + 2\ H_2O = HAsO_4^{2-} + 4\ H^+ + 2\ e^- \quad (12)$$

$$E = 0.881 \text{ volts}$$

$$AsO_2^- + 2\ H_2O = HAsO_4^{2-} + 3\ H^+ + 2\ e^- \quad (13)$$

$$E = 0.609 \text{ volts}$$

The four reactions based upon the possible speciation combinations of arsenic and chlorine are given below.

a. $2.2 < pH < 6.98$

$$HAsO_2 + HOCl + H_2O = H_2AsO_4^- + 2\ H^+ + Cl^- \quad (14)$$

$$E = 2.156 \text{ volts}$$

$$\Delta G = -416.2 \text{ kJ } (-99.43 \text{ kcal})$$

$$K = 7.869 \times 10^{72}$$

b. $6.98 < pH < 7.5$

$$HAsO_2 + HOCl + H_2O = HAsO_4^{2-} + Cl^- + 3\ H^+ \quad (15)$$

$$E = 2.371 \text{ volts}$$

$$\Delta G = -457.72 \text{ kJ } (-109.35 \text{ kcal})$$

$$K = 1.474 \times 10^{80}$$

c. $7.5 < pH < 9.2$

$$HAsO_2 + OCl^- + H_2O = HAsO_4^{2-} + Cl^- + 2\ H^+ \quad (16)$$

$$E = 1.781 \text{ volts}$$

$$\Delta G = -343.82 \text{ kJ } (-82.14 \text{ kcal})$$

$$K = 1.659 \times 10^{60}$$

d. $9.2 < pH < 11.5$

$$AsO_2^- + OCl^- + H_2O = HAsO_4^{2-} + Cl^- + H^+ \quad (17)$$

$$E = 1.509 \text{ volts}$$

$$\triangle G = -291.34 \text{ kJ } (-69.60 \text{ kcal})$$

$$K = 1.063 \times 10^{51}$$

These calculations show that the oxidation of arsenic is potentially very energetic at all pH values from 2.2 to 11.5 and that these reactions posess very large equilibrium constants, K. At concentrations normally encountered, the reaction is even more favorable. For a chlorine concentration of 1.0 mg/L, chloride concentration of 70 mg/L, an As(III) concentration of 100 ppb, an As(V) concentration of 0.1 ppb, and at pH equal to 8.0, the potential is 1.72 volts.

A method to see the theoretical sensitivity of the oxidation reaction by chlorine is to examine the reaction potentials instead of the standard reaction potentials. The following assumptions were made in order to solve the equations: [As(III)] = [As(V)] , 1.0 mg/L chlorine as either HOCl of OCl^- , and no attempt to account for the differences in concentration of the species as the pH approached the pK values. Figure 4 shows the reaction potentials and G values as a function of pH for different Cl^- concentrations. As the pH increases, the reaction potentials and consequently the energies of reaction decrease.

REACTION MECHANISMS

Redox reactions are electron transfer reactions, but these electron transfers are not accomplished in the same manner for all reactions. Taube [65] suggests classifying redox reactions into the following catagories: inner-sphere activated complex, outer-sphere activated complex, and a bridge activated complex. For the inner-sphere mechanism, electron transfer occurs within a single primary bond system. While for the outer-sphere mechanism, electron transfer occurs from one primary bond system to another. In this case, both the oxidizing and the reducing agents are inert to substitution and the electron transfer takes place between ions of similar geometry. For the bridged type reaction, at least one reactant undergoes rapid substitution thereby forming a ligand which bridges the reacting species. The bridging ligand may facilitate electron transfer in two ways termed "chemical" and "resonance". The "chemical" mechanism is a process in which either the oxidizing ion is strong enough to oxidize or the reducing ion is strong enough to reduce the shared ligand whereby the electron deficit or excess is passed to the reducing or oxidizing ion, respectively. In other words, the electron hops from the reducing center to a specific bound state in the ligand to the oxidizing center where it remains. In "resonance" transfer the electron never occupies a well bound state on the ligand. For both types of transfer, the rate of electron transfer is sensitive to the nature of the ligand. This ligand determines the height of the energy barrier that the electron must

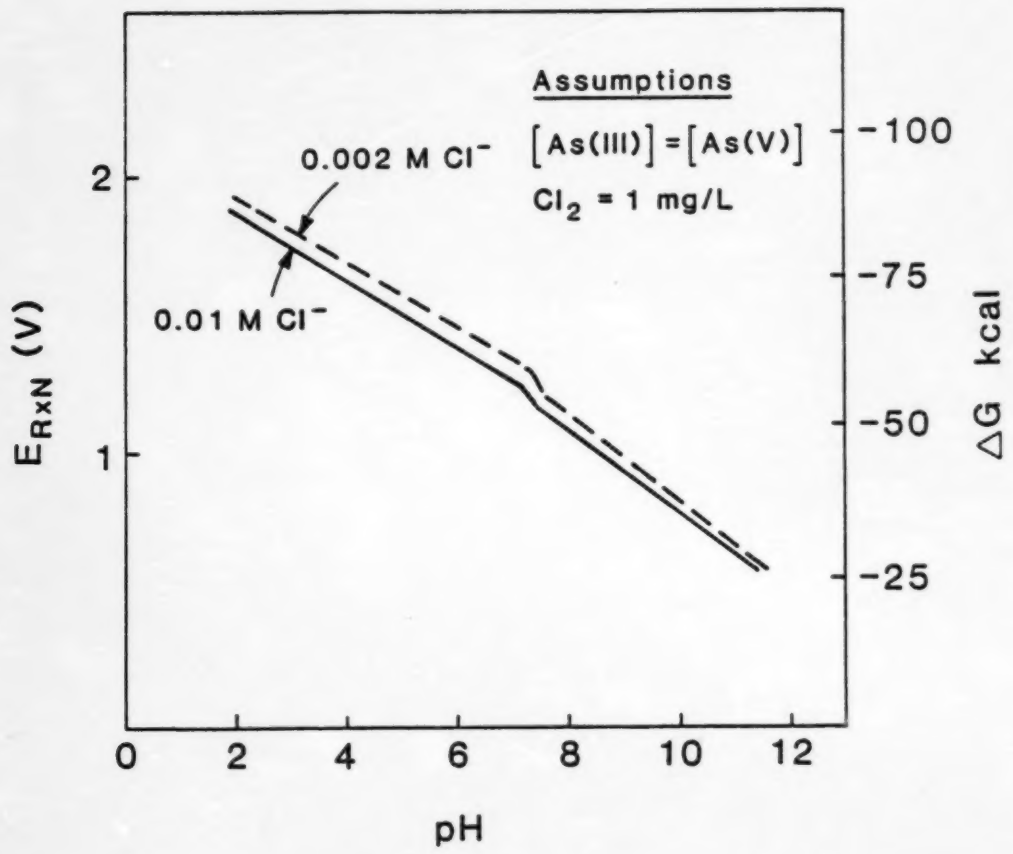

Figure 4. The calculated reaction potential of the oxidation of As(III) by 1.0 mg/L chlorine dosage as a function of pH.

penetrate; thereby determining the probablity of transfer.

HOCl may act as an electrophilic reagent with either oxygen or chlorine as the center of reaction. J. E. Draley [18] suggests that HOCl is an electrophile in which the chlorine atom partially assumes the characteristics of Cl^+ and combines with an electron from solution. Either simultaneously or subsequently, hydroxyl ion is split off. The transfer of Cl^+ is facilitated by a negative charge, the basic part of the molecule. The same type of attack is thought to occur at amino-nitrogen.

On the other hand, the Cl atom can have such a greater attraction for electrons that it may be displaced directly as chloride ion. This type of attack seems to occur with inorganic ions. Anbar and Taube [1] proposed such a mechanism for the oxidation of nitrite by aqueous chlorine. Work by Lister [40] supported this mechanism. Halperin and Taube [30] proposed a similar mechanism for the oxidation of sulfite. The oxidation of Fe(II) and Mn(II) and the reaction with hydrogen peroxide are thought to have similar transfers with the displacement of either Cl^- or OH^- as initial steps. However, the exact nature of these initial steps has not been elucidated.

The solvent can play a key role in a redox reaction. The hydration of an ion may significantly affect its suceptibility to redox reactions. The hydration of an ion may either stabilize or destabilize the intermediates. Stabilizing the intermediate lowers the energy barrier thereby facilitating the reaction.

OXYGEN OXIDATION

Theoretically oxygen should be capable of oxidizing trivalent arsenic (see Figure 2). However, this reaction does not appear to occur except very slowly. Latimer [37] proposed that direct oxidation by O_2 proceeds through the formation of the intermediate, hydrogen peroxide. This reaction has a very low potential. Thus, this step becomes the rate determining step for the direct oxidation by oxygen via this mechanism. Furthermore, pH would also be an important variable as it determines arsenic speciation and, therefore, the half reaction potentials.

SECTION 5

EXPERIMENTS

PRELIMINARY COLUMN STUDIES

The objective of the preliminary column studies was to verify the reportedly efficient removal of pentavalent arsenic and the non-removal of trivalent arsenic on activated alumina. Since some ground waters in the United States contain both excess arsenic and fluoride, and activated alumina is known as a successful adsorbent for fluoride, these column studies were conducted on water that contained both fluoride and arsenic.

Column Experiment Design

Two column runs were conducted simultaneously. Each column was constructed from 1/4" ID plexiglass tubing with stainless steel Swagelock fittings at each end. Each column was loaded with 5 mL of conditioned Alcoa F-1 activated alumina (U. S. standard mesh size 24 X 48). The conditioning procedure for activated alumina is given in Appendix 4. Mini-pumps from Milton Roy Model # NS1-33R were used to control the flowrate at 1.7 mL/min for an EBCT of 2.9 minutes. These pumps provided a steady flow rate over the maximum length of the entire column run-- 58 days.

The column feedwater was a synthetic ground water designed to resemble ground water that had been acidified to pH 6.0 with sulfuric acid. This pretreatment creates a sulfate enriched, bicarbonate-free water. An arsenic concentration of 0.100 mg/L was chosen because it is twice the MCL and not uncommon in arsenic contaminated ground waters (e.g. Hanford, CA and San Ysidro, NM). The same line of reasoning applies to the choice of 3 mg/L as the fluoride concentration. The composition of the column feedwater is given in Table 1.

TABLE 1. COMPOSITION OF COLUMN FEEDWATER

Anions	mg/L	meq/L	Cations	mg/L	meq/L
Cl^-	71	2.0	Na^+	210	9.16
SO_4^-	384	8.0	Ca^{2+}	20	1.0
F^-	3.0	0.16			

The influent to each column differed only in the valence state of the arsenic; one column received 0.100 mg/L As(V), while the other received 0.100 mg/L As(III). The feedwater was made from reagent grade sodium fluoride, sodium chloride, calcium chloride, and sodium sulfate. The pH was adjusted to pH 6 with sulfuric acid. For the As(V), column the feed water was made in 40-liter batches. For the As(III) column, the feedwater with the exception of arsenic addition was also made in 40-liter batches. In order to avoid arsenic oxidation during the long run, freshly prepared trivalent arsenic was added to a 4-liter aliquot each morning for the day's feedstock.

An ISCO Model # 1850 fraction collector was used to collect 25.5-mL samples every 15 minutes. Various 25.5-mL samples were analyzed for arsenic content with a Perkin-Elmer Model 5000 Atomic Adsorption Spectrophotometer with a graphite furnace, Zeeman background correction, and a HGA-400 Furnace Temperature Programmer. An electrodeless discharge arsenic lamp was used as the source lamp. Details of this analysis are given in Appendix 5. Flouride analyses were conducted using an Orion, fluoride ion-selective electrode Model # 94-09-00 with an Orion 501 digital pH/ion analyzer.

OXIDATION STUDIES

Objectives

The oxidation studies were undertaken with the following objectives in mind:

(1) to examine the kinetics of arsenic(III) oxidation by chlorine.

(2) to examine the effect of pH on the oxidation of arsenic(III) by chlorine.

(3) to examine the effect of anions and cations upon the oxidation of arsenic(III) by chlorine.

(4) to examine the effect of chloramines upon the oxidation of arsenic(III).

(5) to examine the effect of TOC upon the oxidation of arsenic(III) by chlorine.

(6) to investigate the oxidation of arsenic(III) by aerobic conditions.

Reagents

All stock arsenic(V) solutions were prepared according to Standard Methods [62] using reagent grade KH_2AsO_4. All stock arsenic(III) solutions were prepared according to Standard Methods [62] using reagent grade As_2O_3. All arsenic(III) solutions were prepared immediately preceding their use. All other solutions with the exception of chlorine oxidant were prepared using the appropriate reagent grade chemicals. Stock chlorine oxidant was prepared from

a commercial bleach (Chlorox) containing sodium hypochlorite. The titer of this solution was checked immediately preceding use. Analysis showed no arsenic to be present in the bleach. The stock chlorine solution was standardized according to Standard Methods [62].

Procedure Development for Chlorine Oxidation

Ultimately a quenching agent was found to be necessary because the oxidation reaction could not be monitored on a continuous basis. No method was available for instantaneous arsenic speciation and quantification. Methods available for analytical arsenic(III) separation from arsenic(V) include ion exchange, pH controlled arsine generation, and selective extraction. Each of these methods requires subsequent analysis for total arsenic in various fractions. The method chosen for arsenic speciation, ion exchange separation, does not provide instantaneous separation. The method chosen for speciation is based upon the work of Clifford et al. [15]. Five mL of pretreated, chloride-form IRA-458 (finer than 35 mesh) in a mini-column at a flow rate of 10 mL/min was used to separate As(III) from As(V) in a 100 mL sample. Under these conditions, the fastest possible speciation time was greater than 10 minutes. Verification experiments with known arsenic standards showed good results as seen in Table 2. Arsenic was analyzed by GFAA as described earlier.

TABLE 2. VERIFICATION OF ARSENIC SEPARATION

Sample	% Expected Recovery	
	As(III)	As(V)
100 ppb As(III)	97	--
50 ppb As(III)/50 ppb As(V)	102	98
100 ppb As(V)	--	98

An indirect method to monitor the oxidation reaction of As(III) by chlorine is to measure the disappearance of chlorine. In addition to the inherent disadvantage of an indirect method, two other disadvantages arose:

(1) Arsenic(III) can be the only species present that exerts a chlorine demand.

(2) The colorimetric methods for free chlorine determination proved to be not sensitive enough.

In experiments with 1.0 mg/L chlorine and 100 ppb As(III) in 0.01 M NaCl, the DPD colorimetric method [62] showed no significant difference between a blank of 1.0 mg/L chlorine and the oxidation samples after 1, 2, 5, 10 minutes

contact time. Furthermore, the adsorbance of a given sample changed over a time span of several minutes (see Appendix 6). The color change was visible; the color changed from an initial reddish color to a deep purple color often within 60 minutes.

As continuous monitoring of the reaction proved unfeasible, oxidation was conducted in batch reactors each sampled at a different time. The batch reactors were 2-L polyethylene beakers filled with 1-L of solution. In oxidation tests on 100 ppb As(III) in DI water by 1.1 mg/L chlorine, samples taken at 1, 5, 15, 30 minutes then separated (10 minutes) had no detectable arsenic(III) remaining (see Table 3).

TABLE 3. OXIDATION IN DI WATER WITH NO QUENCHING

Time	As(III) Remaining
1 minute	< 1 ppb
5	0
15	< 1
30	0

Therefore, a quenching agent was needed because the reaction time of the oxidation reaction was faster than the minimum separation time of 10 minutes. Several criteria were required of the quenching agent.

(1) The quenching agent must react with chlorine instantaneously in a mannner to prevent further oxidation of As(III).

(2) The quenching agent cannot oxidize As(III) nor reduce As(V).

(3) The quenching agent must not deleteriously effect the separation procedure.

(4) The quenching agent should not substantially interfere with arsenic analysis by GFAA.

Ammonia Quenching--

Ammonia, at first glance, appeared to be a good candidate for a quenching agent. It reacts very fast with chlorine to form monochloroamines and was unlikely to oxidize As(III) or reduce As(V), or interfere with the arsenic separation or analysis procedures. However, previous success in using the addition of ammonia and the subsequent formation of chloroamines as a quenching agent for the oxidation of Se(IV) [4] and Cr(III) [14] by chlorine did not follow for the oxidation of As(III). Oxidation of 100 ppb As(III) in

DI water occured in the initial presence of 1.0 mg/L chlorine and a 20 molar excess of NH_3(added as NH_4-Cl). These results are in Table 4.

TABLE 4. SCREENING OF AMMONIA QUENCHING

Sample	Time	As(III) Remaining
control	30 sec	43
control	1 min	39
blank	1 min	98

Thiosulfate Quenching--

Thiosulfate, a common dechlorinating agent, was also considered for use as a quenching agent. However, the reaction of chlorine with thiosulfate was reported to occur in a somewhat slow stepwise fashion [71]. In view of the apparent ease of oxidation of As(III), thiosulfate was abandoned as a potential quenching agent without performing any experiments. Furthermore, thiosulfate proved to be unsuccessful in the quenching of Se(IV) oxidation by chlorine apparently by interfering with the separation by ion exchange [4].

Sodium Sulfite Quenching--

Sodium sulfite is another common dechlorinating agent. It is reported to react instantaneously with chlorine [71]. However, experiments indicated that As(V) was reduced in the presence of a three times excess of sodium sulfite based upon a 1.0 mg/L Cl_2 dosage. The results of these experiments are summarized in Table 5.

TABLE 5. SODIUM SULFITE RESULTS

Sample	As(III) Recovered, ppb
100 ppb As(V)	18
100 ppb As(III) with 1.0 mg/L Cl_2	98
100 ppb As(V) with 1.0 mg/L Cl_2	14
50 ppb As(III)/50 ppb As(V)	61

DPD Quenching--

DPD, N,N-diethyl-p-phenylene diamine oxalate, which is used in the colorimetric test for chlorine, is reported to react instanteously with free chlorine under the proper conditions. The color change associated with the DPD reaction with chlorine can be seen immediately upon addition of DPD reagent under the proper conditions. This reaction is one-to-one, follows Beer's Law and results in the destruction of free chlorine. Furthermore, DPD is unlikely to oxidize As(III) or reduce As(V). Therefore, DPD was a likely candidate as a quenching agent.

A standard DPD solution [62] has a pH of approximately 2 because of the addition of sulfuric acid to promote dissolution. In order to keep the pH in the range 6.2 to 6.5 a phosphate buffer is used in the procedure for the determination of chlorine. Initial experiments with this quenching method were conducted using a standard DPD solution and a standard phosphate buffer solution [62], 5 mL each per 100 mL of sample. However, these experiments could not be analyzed successfully for arsenic. The peak height absorbance was drastically reduced. Suspicion that the phosphate buffer was primarily responsible was confirmed by addition of 5 mL of phosphate buffer to 100 mL of arsenic standard. In order to reduce interference, the amount of phosphate buffer added was reduced 10 fold and the pH adjusted to the correct range with 1 N NaOH (or, in the case of extremely high initial pH, with 1 N HCl). Jar tests were conducted to determine the amount of NaOH solution to be added for each initial pH. Once these amounts were determined (see Table 6), they were used consistantly. This procedure allowed the arsenic analysis by GFAA to be performed satisfactorily. As shown in Table 7, DPD appeared to quench the oxidation reaction and neither oxidize As(III) nor reduce As(V).

TABLE 6. AMOUNTS OF NaOH ADDED FOR QUENCHING

Initial pH	1 N NaOH, mL
5.5	1.5
6.5	1.5
7.5	1.5
8.5	1.0
11.5	0.0
12.5	1.5 (1 N HCl)

TABLE 7. DATA ON DPD QUENCHING

Sample	As(III) Remaining, ppb
100 ppb As(III)	97
100 ppb As(III) with Cl_2 and quenching agents	98
50 ppb As(III)/50 ppb As(V) with Cl_2 and quenching agents	51

For a dosage of 1.0 mg/L chlorine in an oxidation test, the quenching dosage of DPD was at 4.3 molar excess. Further details are given in Table 8.

TABLE 8. REAGENTS

Reagent	Concentration	
	meq/L	mol/L
$H_2PO_4^-$	0.34	0.34
HPO_4^{2-}	0.34	0.17
Cl_2	2.8×10^{-5}	2.8×10^{-5}
DPD	1.2×10^{-4}	1.2×10^{-4}

The DPD was added under conditions of extremely turbulent mixing in order to achieve rapid dispersion. The color change that DPD underwent proved beneficial in monitoring the effeciency of rapid mixing.

Mixing tests were conducted to determine if As(III) oxidation occured during mixing. No detectable oxidation took place after 60 minutes of rapid mixing. These results are presented in Table 9.

TABLE 9. MIXING TEST DATA

Stirring Speed	Time of Mixing,min	Percent As(III) Recovered
low	1	98
med	1	98
high	1	98
high	2	97
high	5	97
high	10	98

Chlorine Oxidant Experiments

An artifical ground water, composition given in Table 10, was used as background water for the oxidation test except where otherwise noted.

TABLE 10. BACKGROUND WATER

Anions	meq/L	mg/L	Cations	meq/L	mg/L
SO_4^{2-}	2.0	96	Na^+	10.0	230
HCO_3^-	6.0	366			
Cl^-	2.0	71			

The pH was adjusted, if needed, by dropwise addition of either 0.1 n HCl or 1.0 N NaOH solution. All pH measurements were made with an electrode calibrated on using two buffers bracketing the expected pH value. An initial arsenic(III) concentration of 100 ppb was chosen because it is twice the MCL and is not an uncommon concentration in arsenic contaminated ground waters. A chlorine dosage of 1.0 mg/L was chosen for the batch tests because there was low chlorine demand in the artifical ground water and the dosage was sufficient for reaction completion. The batch chlorine oxidation tests were conducted in 2-L polyethylene beakers with 1-L sample size. A propeller mixer provided rapid mixing for the addition of stock chlorine solution and quenching agent. The shaft and impeller were plastic coated. All time increments were measured with a laboratory timer. A 100-mL pipette was used to collect the sample which was immediately separated. An initial sample and the As(III) fraction were stored in a 60-mL and 125-mL respectively polyethylene bottles for subsequent GFAA analysis. An occasional As(V) fraction was collected as a spot check of separation recovery; otherwise, As(V) was determined by difference.

Oxygen Oxidant Tests

Some oxygen oxidation tests were conducted on various background waters containing 100 ppb As(III). For all these experiments, a 500 mL sample in a Pyrex gas washing bottle, Model # 31760 was bubbled with O_2 at a flow rate of 300 to 400 mL/minute for 60 minutes. One sample to serve as a blank was bubbled with nitrogen under these same conditions.

In another experiment, arsenic(III) containing samples were allowed to sit in 125 mL polyethylene bottles with air in the headspace for 61 days. Samples were 200 ppb As(III) in DI water at pH 6.0, 7.0, and 8.0; 50 ppb As(V)/ 50 ppb As(III) in DI water at pH 6.0, 7.0, and 8.0; and 50 ppb As(III)/ 50 ppbAs(V) in artificial groundwater with 1 meq Ca^{2+} (composition given in Table 11) at pH 7.3 and 8.3.

TABLE 11. BACKGROUND WATER WITH CALCIUM

Anions	meq/L	mg/L	Cations	meq/L	mg/L
SO_4^{2-}	2.0	96	Na^+	9.0	207
HCO_3^-	6.0	366	Ca^{2+}	1.0	20
Cl^-	2.0	71			

SECTION 6

RESULTS AND DISCUSSION

COLUMN STUDIES

The effluent history from the As(III) column is shown in Figure 5, and the effluent history from the As(V) column is shown in Figure 6. As Figure 5 shows, effluent trivalent arsenic concentration reaches the MCL much sooner than fluoride (300 and 1600 bed volumes, respectively), indicating that fluoride is a more preferred species than trivalent arsenic. This result is expected because, at the influent pH of 6.0, trivalent arsenic is predominantly non-ionic arsenious acid. As Figure 6 indicates, effluent arsenic(V) reached the MCL significantly later than fluoride breakthrough, i.e. 23,400 and 1550 bed volumes, respectively. This behavior was expected because arsenate is a more preferred species than fluoride and on a milliequivalent basis the As concentration is much lower than fluoride--0.00135 meq/L compared to 0.158 meq/L.

As shown in Figure 7, a comparison of the arsenite versus arsenate breakthrough curves, As(III) reached the MCL almost immediately at 300 bed volumes(0.6 days), while As(V) did not reach the MCL until 23,400 bed volumes (48 days). Thus, the presence of pentavalent arsenic results in column runs nearly 80 times longer than trivalent arsenic. Therefore, pre-oxidation of As(III)-containing waters is essential for efficient treatment using activated alumina.

Even though trivalent arsenic appeared in the effluent very quickly, some arsenic (III) was removed. In fact, at 90 percent of equilibrium, a mass balance showed that 0.344 mg As(III) had been removed yielding an approximate mass loading of 0.078 mg As(III)/ g alumina. Speciation of the influent and the effluent showed the arsenic to be totally As(III). Therfore, it is the trivalent species that is actually absorbed onto the alumina, assuming no oxidation of As(III) occured.

The comparatively poor removal of As(III) versus As(V) is not suprising in light of alumina surface chemistry and of arsenic speciation. Alumina is an amphoteric ion exchanger, capable of both anionic and cationic exchange [34]. In acidic solutions, surface-bonded protons are electrically balanced by anions adsorbed. In basic solutions, cations are electrically balanced by surface-bonded anions. Hydroxide ions are highly preferred as counterions to the adsorbed protons in neutral and slightly acidic solutions. Other anions such as fluoride and arsenate must compete with hydroxide for ion-exchange sites.

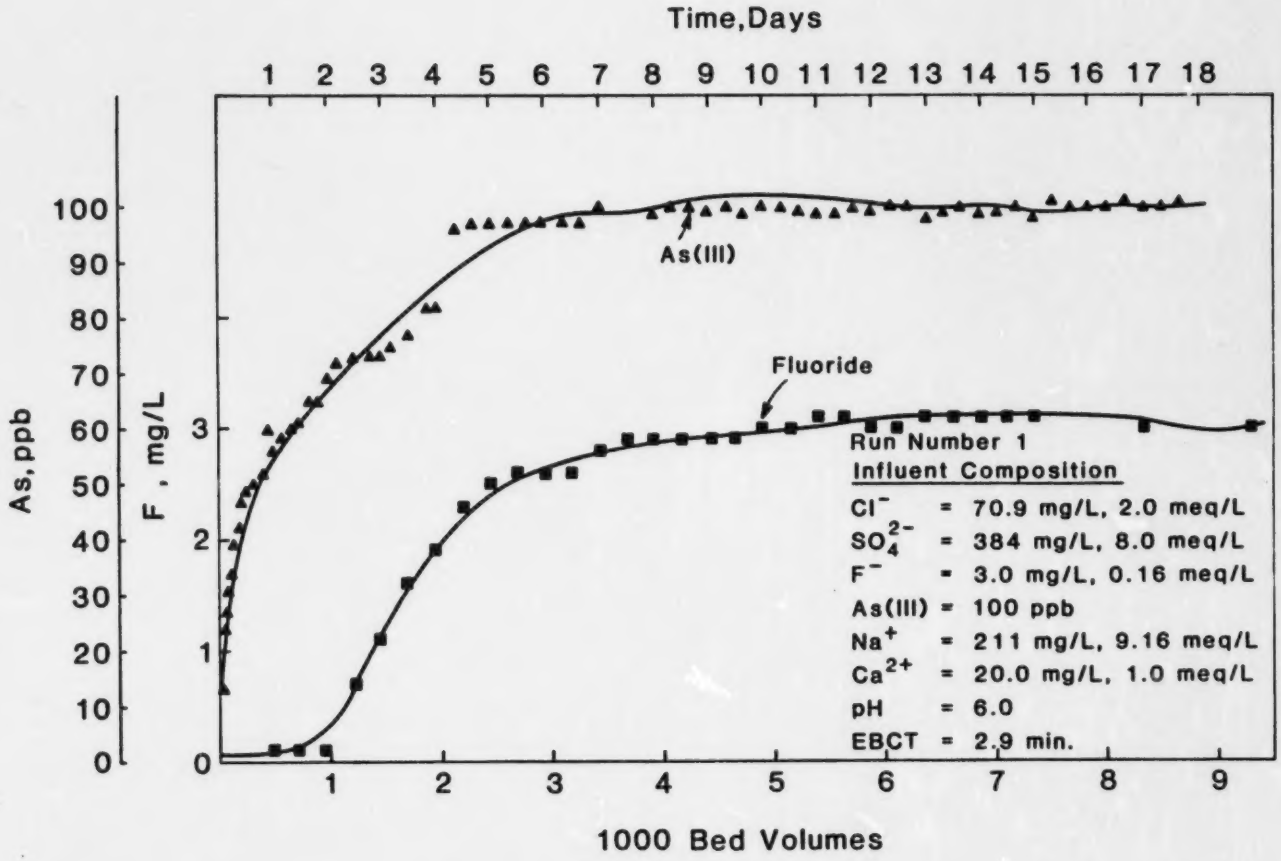

Figure 5. Arsenite, As(III), and fluoride breakthrough curves from a minicolumn containing 28 X 48 mesh, F-1 activated alumina.

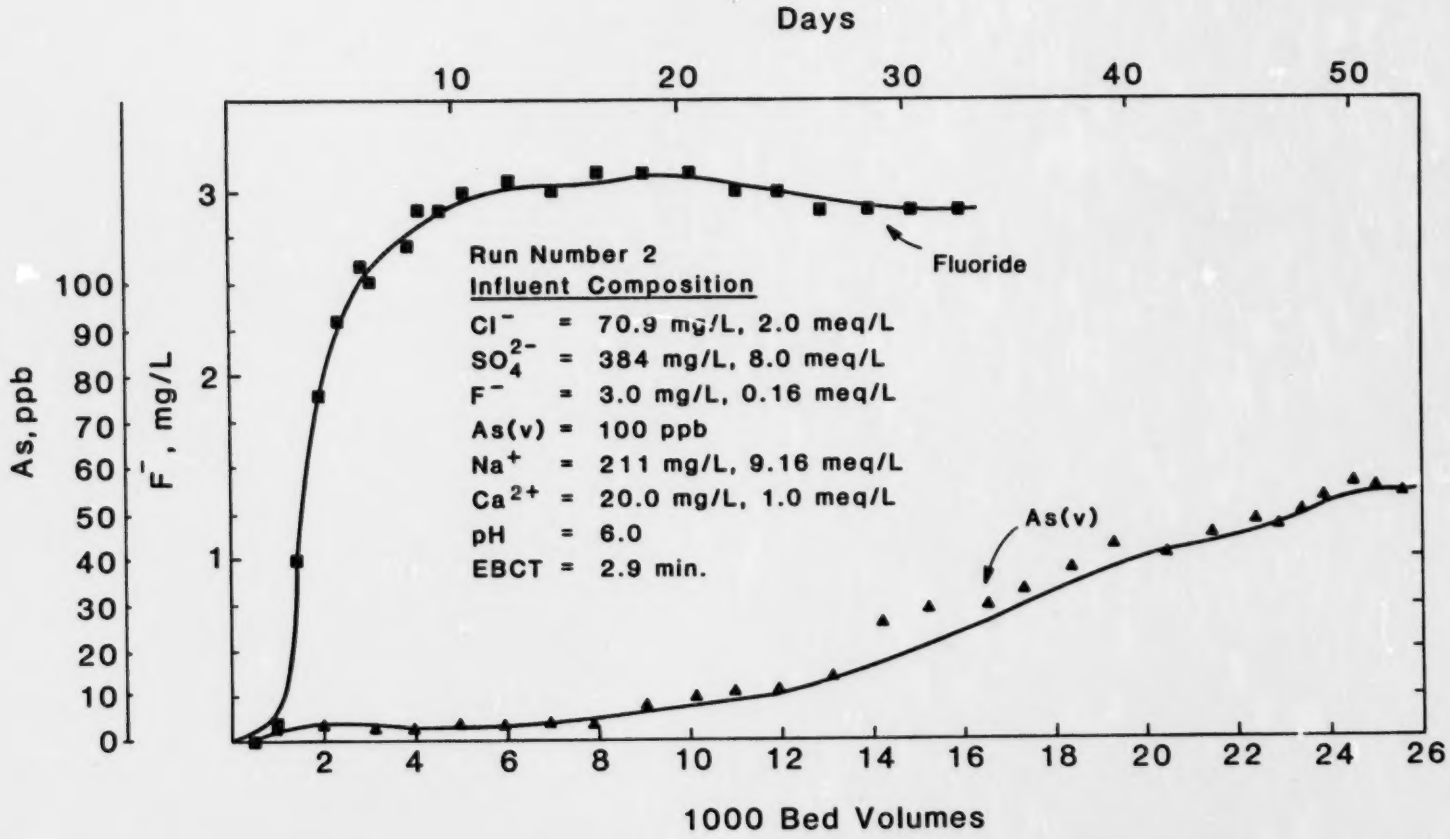

Figure 6. Arsenate, As(V), and fluoride breakthrough curves from a minicolumn containing 28 X 48 mesh, F-1 activated alumina.

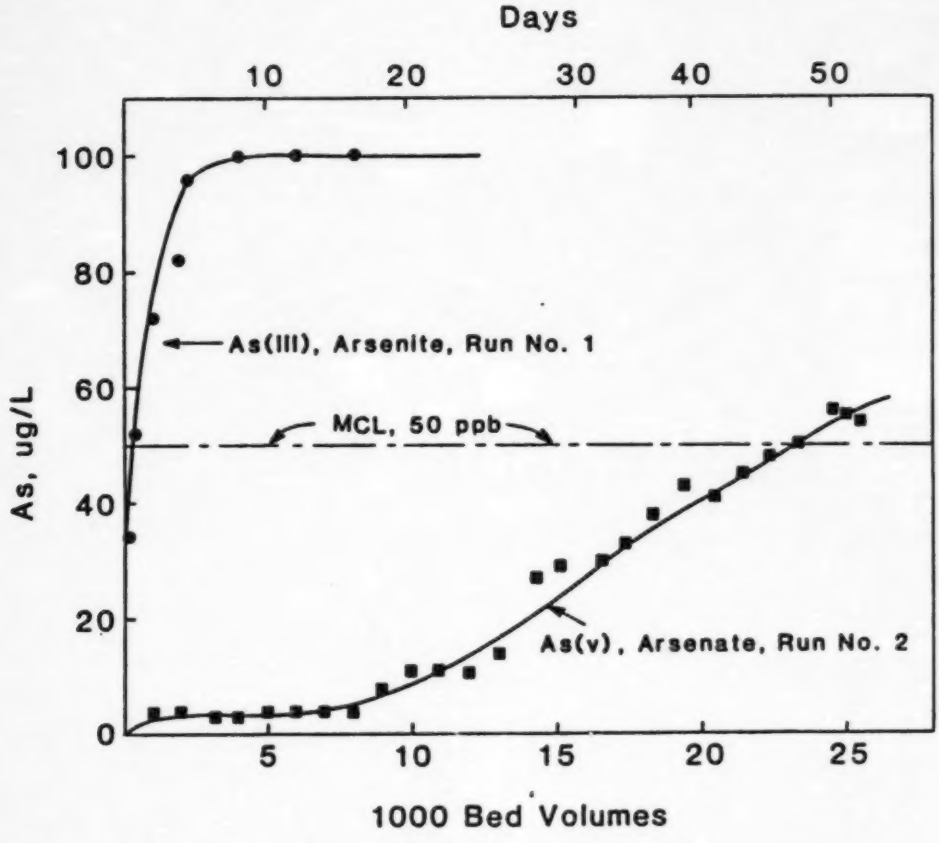

Figure 7. Comparison of As(III) and As(V) breakthrough curves from minicolumns of activated alumina. C_T = 100 ppb. EBCT = 2.9 min. pH = 6.0

In fact, a generally accepted selectivity sequence for anion adsorption (or ion exchange) on alumina exists [6, 67, 68]. This sequence is presented below:

$$OH^- > HPO_4^{2-}, HAsO_4^{2-} > F^- > Si(OH)_3O^- > CrO_4^{2-} > Cl^- >$$

$$NO_3^- > MnO_4^- > ClO_4^- > CH_3COO^-$$

At the column influent pH of 6.0, trivalent arsenic exists predominantly (1000:1) as the non-ionic species--arsenious acid. However, as Figure 8 shows, at the influent conditions (pH = 6.0, 0.100 mg/L As(III)), the hydroxyl ion concentration is ten times greater than the arsenite anion concentration. An arsenic mass balance on Run 1 showed that 0.344 mg As(III) was adsorbed; however, only 0.0001 mg As(III) was available as the anion of arsenious acid to be adsorbed. Therefore, it is unlikely that ion exchange is the only mechanism of adsorption of As(III) because more arsenic was adsorbed than existed as the anion. Furthermore, at pH 6.0 the arsenite anion always exists in concentrations less than the concentration of the more preferred hydroxyl ion.

Unlike trivalent arsenic, pentavalent arsenic exists predominantly as the singly-charged anion, $H_2AsO_4^-$. As Figure 9 shows, at pH 6.0, this species concentration is 100 times that of the highly preferred hydroxyl ion. Even the doubly-charged anion, $HAsO_4^{2-}$, exists at over 10 times the concentration of the preferred hydroxyl ion. Thus, based on concentration, As(V) can compete favorably for the available adsorption sites.

As indicated in Figure 10, fluoride adsorption was little affected by the difference in adsorption of As(III) as compared to As(V). The effluent concentration of fluoride reached the MCL at 1600 bed volumes for the column with As(III) and at 1500 bed volumes for the column with As(V). Although As(V) is more preferred than fluoride and As(III) is less preferred, the difference in arsenic adsorption is unlikely to effect fluoride adsorption. This situation occurs because the molar ratio of F^-/As is 117. Thus, arsenic would typically occupy only one site for every 117 sites occupied by fluoride, if the selectivities were equal.

Studies on arsenic and fluoride removal were conducted in San Ysidro, NM using the University of Houston/EPA Mobile Drinking Water Treatment Research Facility [16]. The fluoride and total arsenic effluent histories from that work are presented in Figure 11. Their column was 1" ID filled with Alcoa F-1 activated alumina (mesh 24 X 48). A comparison of results from the field and laboratory data are presented in Table 12. Although the bed volumes to the fluoride MCL were greater in the field study, the capacity to the fluoride MCL was almost exactly the same as the capacity obtained in laboratory tests.

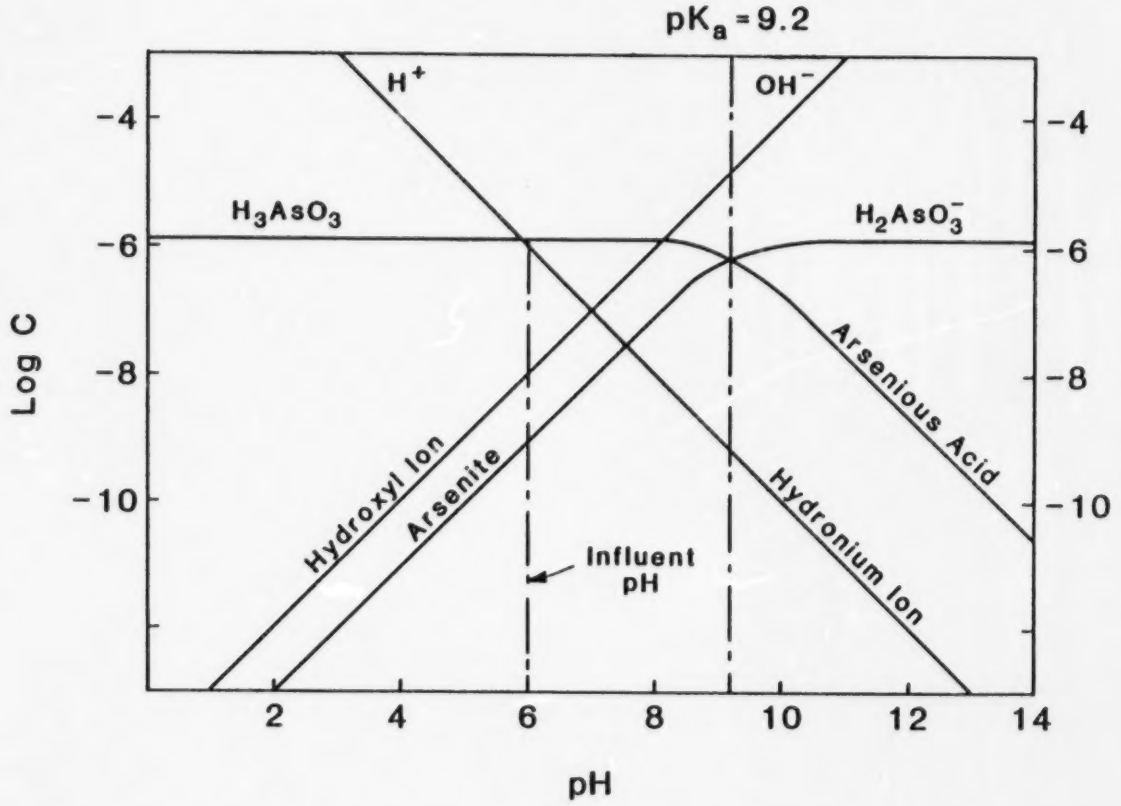

Figure 8. Log concentration vs. pH diagram for arsenious acid, As(III), system. Total As(III) concentration is 100 ppb.

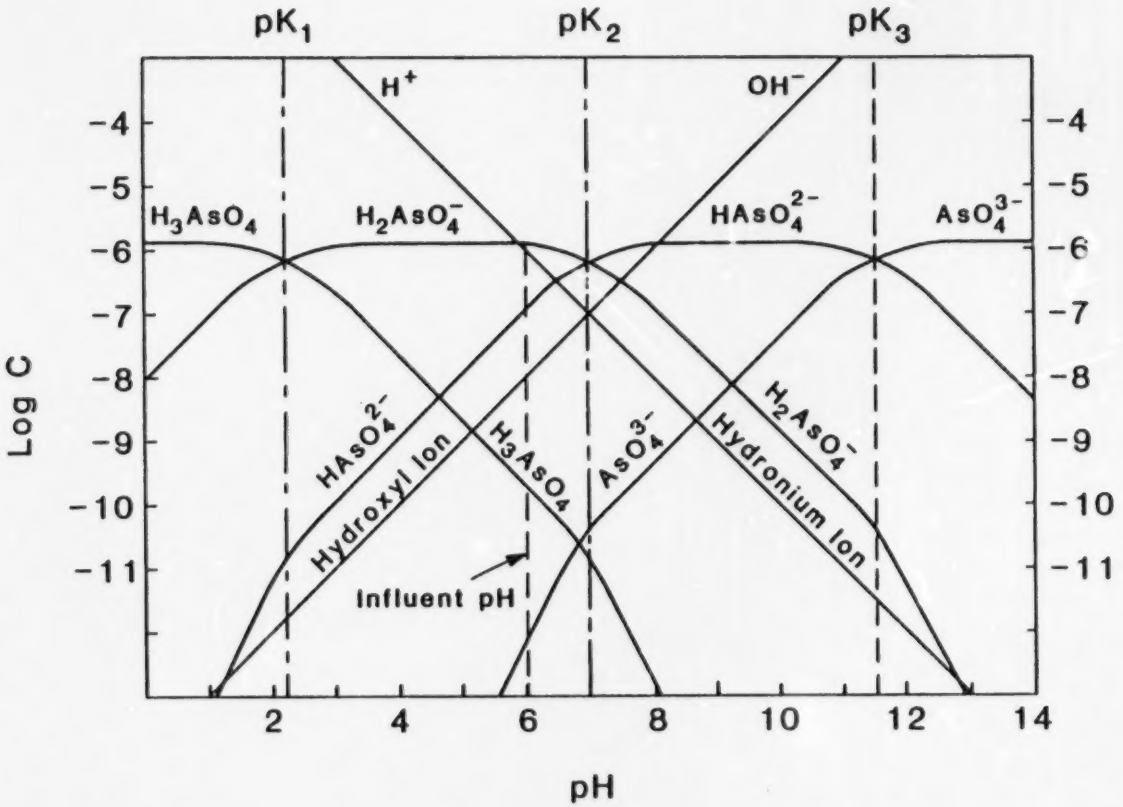

Figure 9. Log concentration vs. pH diagram for arsenic acid, As(V), system. Total As(V) concentration is 100 ppb.

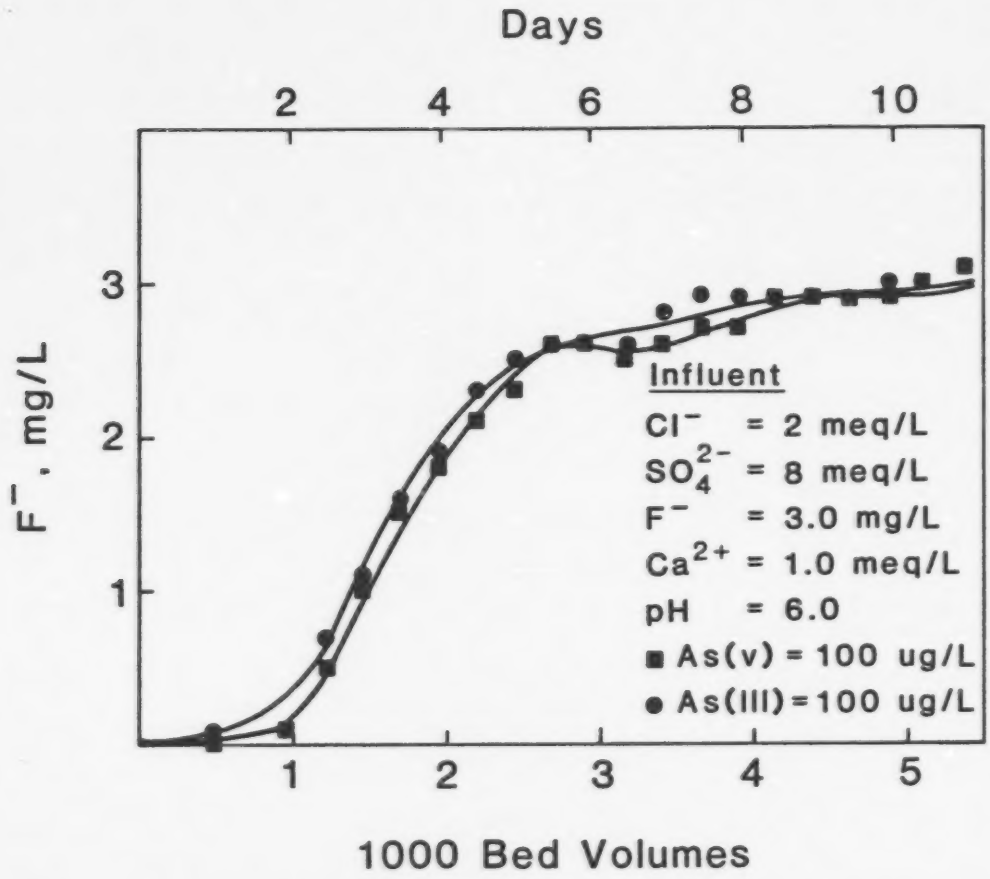

Figure 10. Comparison of fluoride breakthrough curves from mini-columns of activated alumina. C_T = 3.0 mg/L EBCT = 2.9 min

TABLE 12. COMPARISON OF LABORATORY AND FIELD DATA FOR FLUORIDE AND ARSENIC REMOVAL

	UH Laboratory Test		San Ysidro
	As(III)	As(V)	Field Test
BV to As MCL	300	23400	8760
Arsenic capacity, g/cubic m	18	1610	575
BV to F^- MCL	1600	1550	2520
Fluoride capacity, g/cubic m	4190	4280	4160

Notes: The San Ysidro water contained 48 ppb As(V), 32 ppb As(III), and 2.0 ppm fluoride.

Although the influent arsenic concentration differed between the field study and the laboratory study, the arsenic removed per m^3 of alumina in the field was qualitatively in the range expected from the laboratory studies (i.e. greater than 18 g/m^3 and less than 1610 g/m^3). However, the shape of the arsenic breakthrough curve in the field study (see Figure 11) was suprisingly sharp because a much earlier breakthrough of trivalent arsenic was expected. By way of explanation, some oxidation of As(III) to As(V) may have occured in the field column, and the trivalent arsenic concentration of the influent in the field study was only 0.032 mg/L--one third the concentration in the laboratory study. Furthermore, the pentavalent arsenic breakthrough curve in Figure 6 indicated early breakthrough of As(V). This effect was presumably because of the shorter EBCT of the lab column, its shallow bed depth, and the fact that the adsorption zone was a large fraction of the bed depth.

CHLORINE OXIDANT STUDIES

Kinetics

The results of the kinetic experiments on the oxidation of arsenic(III) by chlorine in artificial ground water with sodium as the cation are presented in Figure 12. The Figure 12 indicates that the reaction has reached completion by the 5-second data point. However, five seconds is the fastest possible reproducible quenching time using this method. Under the experimental conditions, the data imply that $-d[As(III)]/dt \geq 2.66 \times 10^{-7}$ mol/L sec. Johnson and Bruckenstein [35], in their study on the oxidation of As(III) by electrogenerated iodine at pH 8.2 to 9.2, reported a maximum overall rate $-d[As(III)]/dt$ of approximately 7 mol/L sec. Chlorine oxidant is considered a more powerful oxidizing agent than iodine since it is capable of oxidizing iodine. Assuming the oxidation of As(III) by chlorine follows a rate

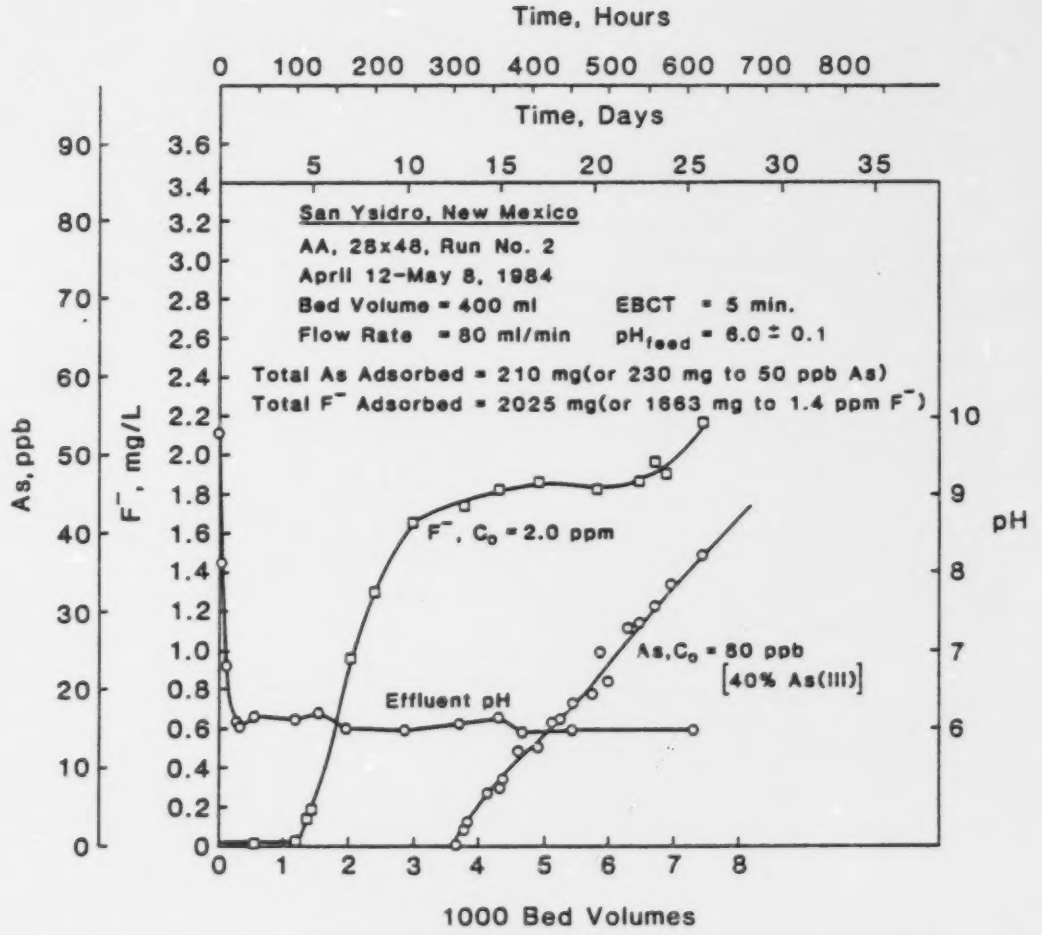
Time, Hours
0 100 200 300 400 500 600 700 800
Time, Days
5 10 15 20 25 30 35
San Ysidro, New Mexico
AA, 28x48, Run No. 2
April 12-May 8, 1984
Bed Volume = 400 ml
EBCT = 5 min.
Flow Rate = 80 ml/min
pH feed = 6.0 ± 0.1
Total As Adsorbed = 210 mg(or 230 mg to 50 ppb As)
Total F⁻ Adsorbed = 2025 mg(or 1863 mg to 1.4 ppm F⁻)
As, ppb
F⁻, mg/L
pH
F⁻, C0 = 2.0 ppm
As, C0 = 80 ppb
[40% As(III)]
Effluent pH
1000 Bed Volumes

Figure 11. Total arsenic and fluoride breakthrough from 1 inch column in San Ysidro, NM.

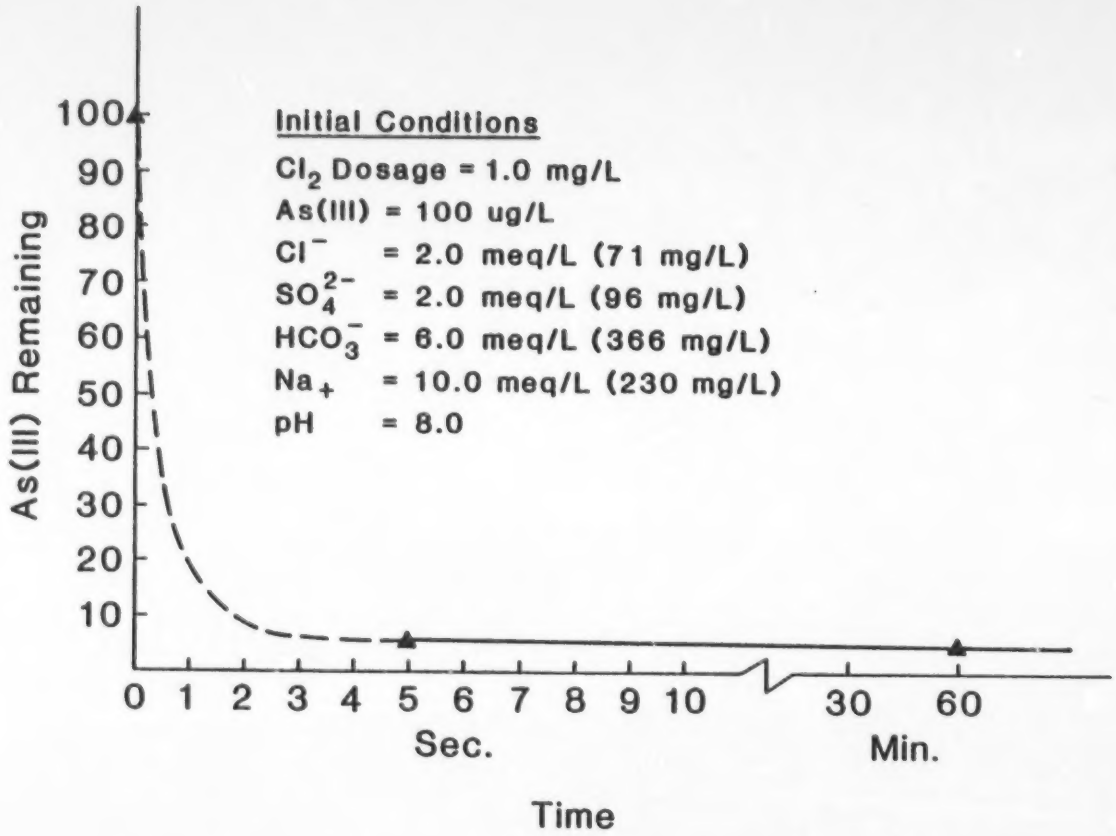

Figure 12. The oxidation kinetics of 100 ppb As(III) using 1.0 mg/L chlorine with DPD quenching.

expression of the form

$$- d[As(III)] / dt = k [As(III)]^m [Cl_2]^n \quad (1)$$

where $[As(III)] = [H_3AsO_3] + [H_2AsO_3^-]$, and $[Cl_2] = [HOCl] + [OCl^-]$, the only variables available for manipulation are [As(III)] and $[Cl_2]$. In American water treatment, chlorine dosages less than 1.0 mg/L are not often practiced. Increasing the arsenic concentration 10^4 times to 1000 mg/L, an unrealistic ground water concentration, would only allow the determination of $-d[As(III)]/dt \leq 2.66 \times 10^{-3}$ mol/L sec. For these reasons, further experiments to determine the kinetics were abandoned.

From equilibrium calculations, the oxidation of As(III) to As(V) by chlorine should go to completion; however, as shown in Figure 12, the reaction only goes to approximately 95 percent completion. Although at pH 8.0 equilibrium calculations predict the As(V)/As(III) to be 2.34×10^{77} at these experimental conditions, the reaction appears to reach completion at an As(V)/As(III) ratio of approximately 19. The leakage of 1 ppb As(V) during the analytical separation procedure would automatically give a false As(V)/As(III) ratio of 100; the measured As(III) concentrations shown in Figure 12 may be attributable to leakage of As(V). The apparent 95 percent complete reaction is surely sufficient for water treatment practice. However, other factors may effect the extent of reaction including the pH, and the presence of other ions.

pH Effect

As the pH increases, the speciation of both arsenic and chlorine changes, and the free energy of reaction decreases. The experimentally observed effect of pH on the oxidation of As(III) by chlorine is shown in Figure 13. In the neutral pH range of 6.5 to 9.5, the pH does not significantly effect the extent of reaction. It is not until pH values greater than 10.5 that the oxidation reaction is affected adversely. By pH 11.5 the G of reaction has been approximately halved from the ΔG of reaction at pH 6.5. The relative insensitivity of the oxidation reaction of As(III) to As(V) by chlorine in the neutral pH range may be attributed to the fact that As(III) exists predominantly as arsenious acid in this pH range and that the changes in pH do not significantly affect the activation of the species. Furthermore, from the data it appears that for pH values less than 10.5 that the ΔG of reaction is sufficient with adequate overpotential for the reaction to occur. At pH 11.5, the overpotential necessary for complete reaction may not be available.

The slight decrease in reaction extent at pH 5.5 can be explained by examining the oxidation equation for that pH range:

$$H_3AsO_3 + HOCl = H_2AsO_4^- + 2\ H^+ + Cl^- \quad (2)$$

Even though the ΔG of reaction (2) increases with decreasing pH, this oxidation reaction is acid producing in the 2.2 to 7.0 pH range. As the pH decreases, the H^+ concentration increases representing an accumulation of products. Another contributing factor may be the increase in Cl^- as a result

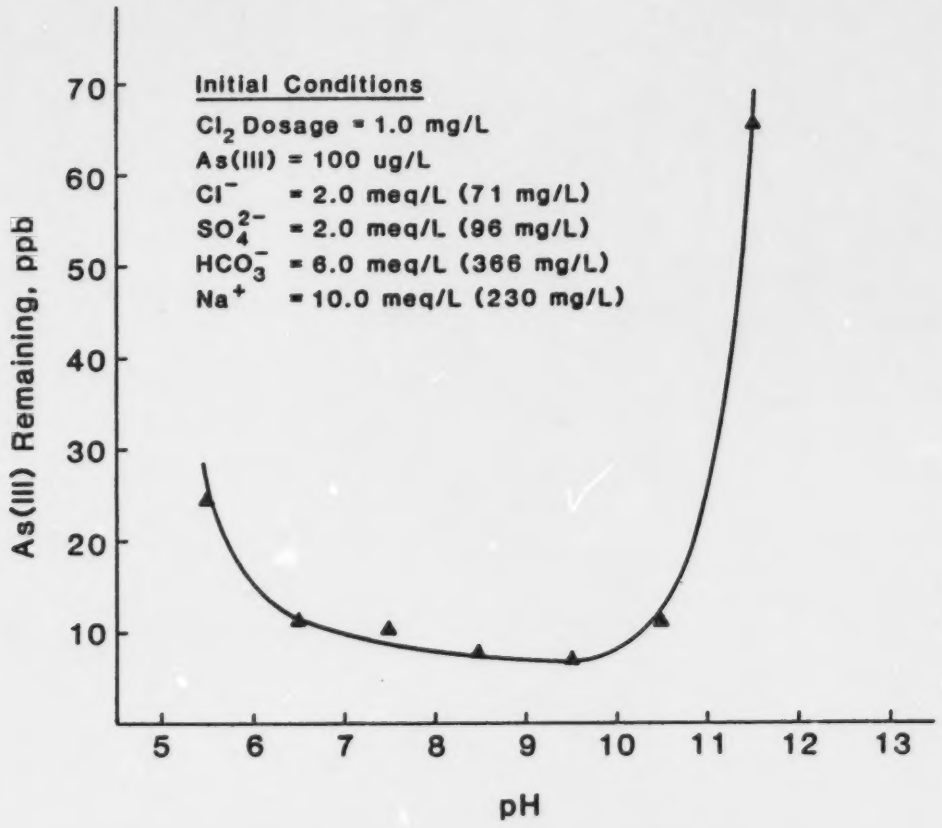

Figure 13. The effect of pH on As(III) oxidation by chlorine with DPD quenching after 30 sec.

of acidification from pH 8.3 with HCl. The effect of background Cl^- is theoretically important and will now be discussed.

Effect of Chloride Concentration

Figure 14 shows the effect of Cl^- on the extent of reaction with either sodium or calcium as the counterion for chloride. The data point at 0.1 M NaCl is falsely high because the high Cl^- concentration drove some As(V) off the ion-exchange resin during separation, and caused a falsely high As(III) value. The curve was drawn to an estimated actual concentration. This estimation was made on the basis of blank separation of 50 ppb As(III)/50 ppb As(V) in 0.1 M NaCl.

As Figure 14 shows, increasing Cl^- concentrations in the background water decrease the extent of oxidation reaction. Although some breakthrough of As(V) may have occured during separation, a real As(III) concentration remains at the 0.02 M data point. The open square represents As(V) leakage from a blank separation of 100 ppb As(V) in 0.02 M Na Cl. Since chloride represents a product of the oxidation, this behavior is qualitatively expected. In DI water, no As(III) is detected. However, at 0.01 M Cl^-, As(III) is detected after oxidation. At pH 6.0 and $[Cl^-] = 0.01$ M, equilibrium calculations predict the As(V)/As(III) ratio to be 2.22×10^{85}. Three possibilities exist to explain this behavior. The first explanation is experimental error in the separation. As(V) leakage during separation may account for the traces of arsenic(III) found after oxidation at salt concentrations up to 0.01 molar. The second explanation is that the published thermodynamic data are in error. Some error in the published thermodynamic data is likely. The calculated pK values using G_f from Latimer [37] for arsenic acid are 3.6, 7.26, and 12.47 while the measured values are reported as 2.2, 7.0, and 12.5. And, Latimer is ultimately the basic source of the thermodynamic data published for arsenic. And although errors in the published thermodynamic literature are possible, it is unlikely to account for the complete difference between the predicted and measured result, especially since the errors in the thermodynamic data seem to be predominantly for the reactions at lower pH values. Chloride ion appears to exert substantial influence on the extent of oxidation at high chloride concentration, although this influence is of insignificant practical value at the chloride concentrations encountered in drinking water treatment.

Furthermore, these data indicate that the increase in As(III) remaining at lower pH values may be in part (approximately 5 ppb) because of the added Cl^- during pre-acidification with HCl. However, the trend of decreasing extent of reaction for pH decreasing below pH 6.5 still appears to hold.

The effect of Cl^- concentration upon arsenic(III) oxidation is very different than its effect upon Cr(III) oxidation. The oxidation of Cr(III) by chlorine is much slower than the oxidation of As(III); the Cr(III) oxidation occurs over several hours at higher chlorine dosages [14]. Furthermore, increasing chloride concentration appears to enhance the reaction, probably because the chloro-Cr(III) complex is more susceptible to oxidation than the insoluble alternative--$Cr(OH)_3$.

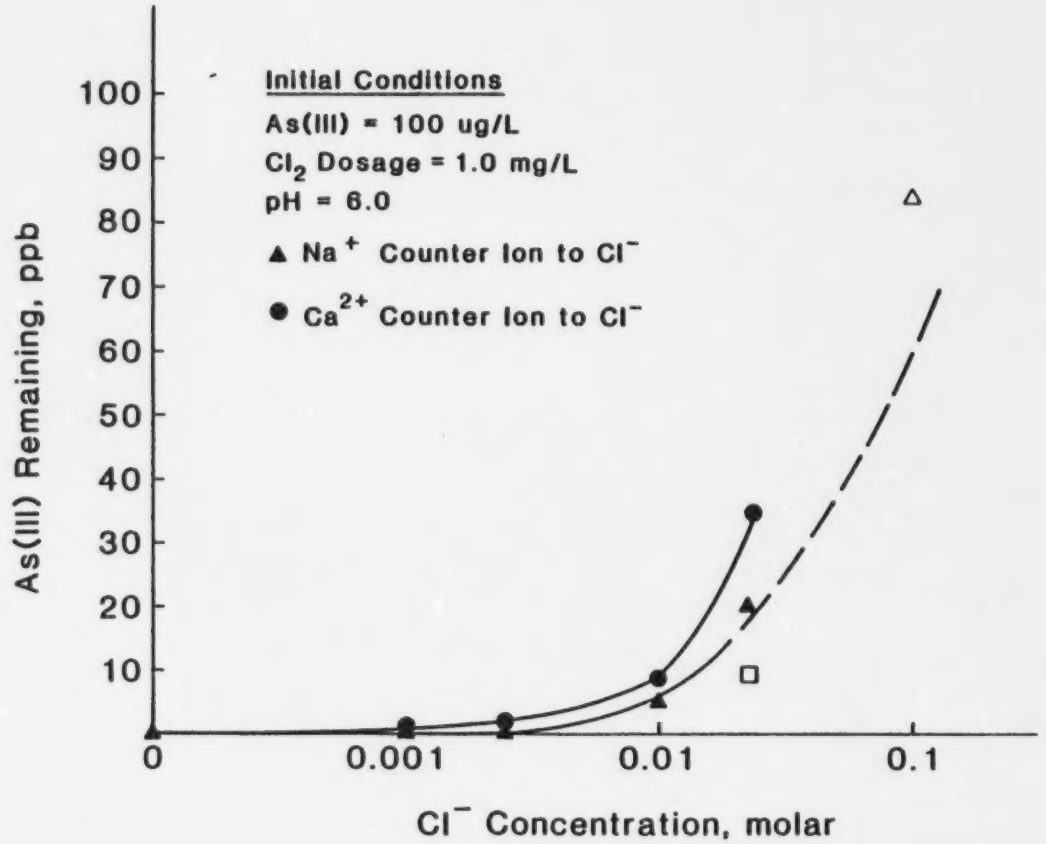

Figure 14. The effect of chloride concentration on As(III) remaining after oxidation using 1.0 mg/L chlorine dosage.

Effect of Counterion

Figure 14 also shows a comparison between the extent of reaction when sodium is the only cation or when calcium is the only cation to chloride. At chloride concentrations encountered in ground water (0.0001 M to 0.01 M), no effect can be attributed to the cation. No real ligand effect can be seen.

Figure 15 shows the kinetics of reaction are not measurably changed in the presence of 1.0 meq/L Ca^{2+}. A comparison of the rate of oxidation in artificial ground water that contains 10 meq/L sodium versus one that contains 9 meq/L sodium and 1 meq/l calcium shows no measurable difference. If the presence of calcium effects the rate of As(III) oxidation to As(V), it is probably of no practical significance for treatment processes.

Effect of Chloramines

Figure 16 shows the kinetics of oxidation of 0.100 mg/L As(III) in artificial ground water containing a dosage of 1.0 mg/L chlorine with a 10 molar excess of ammonium chloride at pH 8.3. These conditions produce monochloramine. This figure has two salient points. First, the reaction appears to reach completion at an As(V)/As(III) ratio of approximately two thirds. And, secondly, the reaction appears to have slower kinetics than the oxidation of As(III) by free chlorine. As expected, analysis of the chloramine species, showed only the presence of NH_2Cl. The following reaction can be written:

$$NH_2Cl + H_3AsO_3 + H_2O = NH_4^+ + HAsO_4^{2-} + Cl^- + 2\ H^+ \qquad (3)$$

Using the free energies of formation given in Appendix 7, this reaction has a standard free energy of -82.4 kcal/mol and an equilibrium constant of 2.57×10^{60}. Thus, as written, the above reaction is possible. Under the experimental conditions, thermodynamic calculations predict an As(V)/As(III) ratio of 5.66×10^{78} at equilibrium. The observed data does not match the predicted value at all. The thermodynamic data available may be somewhat in error as discussed previously. However, these errors are not likely to account for the total difference between observed and predicted values.

One possible explanation is that, although the above reaction is possible, it does not actually occur because the energy barrier of activation is too high. In this case, oxidation is accomplished by analytically undetectable amounts (less than 0.1 mg/L) of free chlorine remaining in solution. The formation of monochloroamine is a reversible reaction; however, the equilibrium occurs in the direction of monochloramine formation. Given the apparent ease of oxidation of As(III) by free chlorine oxidant, very small amounts of free chlorine may be capable of partially oxidizing As(III), as will be quantified later. The hydrolysis reaction of monochloramine to produce free chlorine has only recently been studied [29]. Kinetic data show this reaction to be slow. Current kinetic data indicates that, at 60 minutes, 7 percent of the monochloramine should be hydrolyzed. However, this result was not observed experimentally.

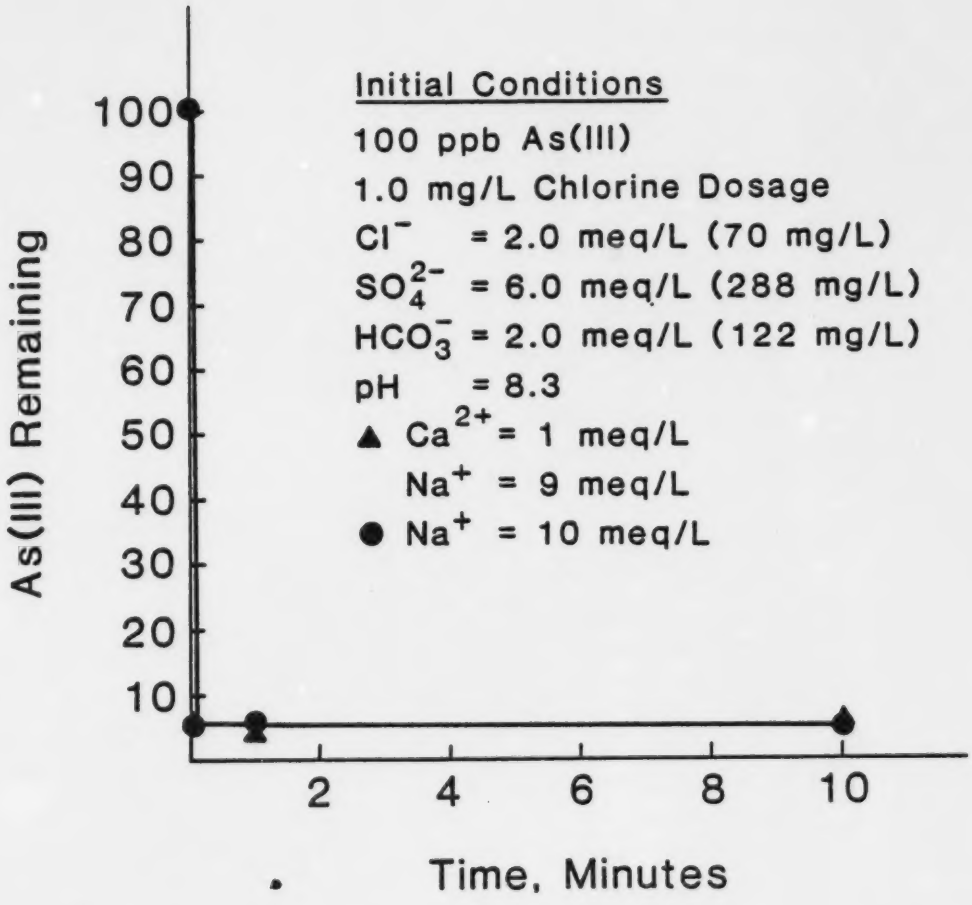

Figure 15. A comparison of the kinetics of oxidation of 100 ppb As(III) by 1.0 mg/L chlorine dosage in the presence of different counterions.

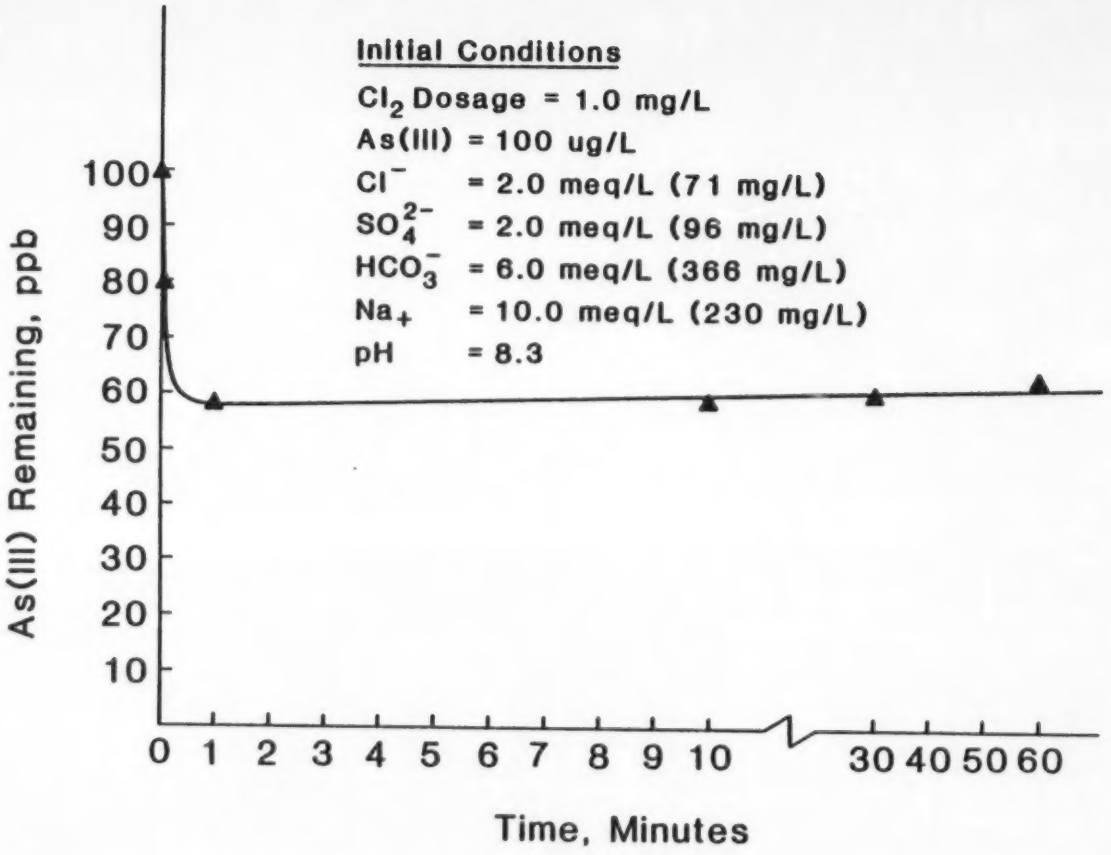

Figure 16. The oxidation kinetics of 100 ppb As(III) by 1.0 mg/L monochloramine in the presence of excess ammonia.

Studies on Se(IV) [4] and Cr(III) [14] showed that they could not be oxidized by chloramines. The following reaction analogous to reaction (3), can be written:

$$NH_2Cl + SeO_3^{2-} + H_2O = NH_4^+ + Cl^- + SeO_4^{2-} \quad (4)$$

This reaction has a standard free energy of reaction of -25.74 kcal/mol with an equilibrium constant of 7.43×10^{18}. It is potentially less energetic than the arsenic reaction. No noticible selenium oxidation occurred in the presence of monochloramine. However, these factors do not necessarily imply that monochloramine is the oxidizing species. The oxidation kinetics of selenium(IV) are much slower than the kinetics of arsenic(III) oxidation, implying that the activation energy of arsenic(III) is much lower than that for Se(IV). As a result the trace amounts of free chlorine may not be capable of detectable Se(IV) oxidation.

Effect of pH on Chloramine Oxidation

As Figure 17 shows, the solution pH does not appear to substantially effect the extent of reaction in the pH range 6.5 to 10.5. This pH sensitivity of the chloramine reaction is very similar to that obtained for oxidation of As(III) by free chlorine (See Figure 13) where a somewhat decreased rate is observed at pH 5.5. The monochloramine formation reaction should be dependent upon pH because of the different species of chlorine and ammonia present at different pH values. The reaction of monochloramine to dichloramine is not considered here because the reaction only occurs at pH less than 6.0. And this reaction occurs only slowly. Calculations from kinetic data show that after 1 hour only 7 percent of the monochloramine has been converted and at the 1 minute quenching time used in this experiment less than 0.1 percent of the monochloramine should be converted to dichloramine at the lowest pH examined. The following reactions are possible:

a. $pH < 7.5$

$$HOCl + NH_4^+ = NH_2Cl + H_2O + H^+ \quad (5)$$

$$\Delta G = -2.62 \text{ kcal/mol}$$

$$K = 83.3$$

b. $7.5 < pH < 9.3$

$$OCl^- + NH_4^+ = NH_2Cl + H_2O \quad (6)$$

$$\Delta G = -12.92 \text{ kcal/mol}$$

$$K = 2.97 \times 10^9$$

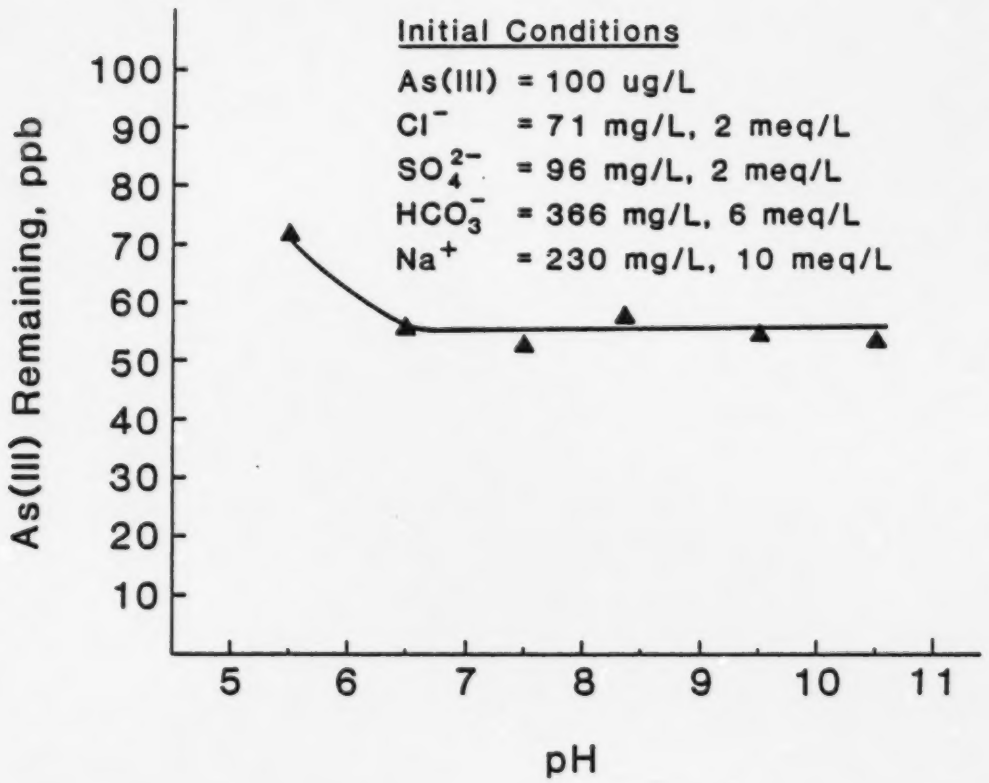

Figure 17. The effect of pH on the oxidation of 100 ppb As(III) by 1.0 mg/L monochloramine and excess ammonia.

c. $9.3 < pH$

$$OCl^- + NH_3 = NH_2Cl + OH^- \quad (7)$$

$$\Delta G = -6.44 \text{ kcal/mol}$$

$$K = 5.27 \times 10^4$$

Reaction (6) implies that in the pH range 7.5 to 9.3 the ratio of monochloramine to chlorine is constant. At experimental conditions, this ratio is equal to 7.5×10^5 for the pH range 7.5 to 9.3 using the given thermodynamic data. At the level of total chlorine used in the experiment, the free chlorine concentration using the given thermodynamic data would be 3.76×10^{-11} molar. This concentration is not nearly enough to oxidize the amount of arsenic observed to be oxidized experimentally if the oxidation occurs on a stoichiometric basis. However, these thermodynamic data may be in error; the values for K and consequently the monochloramine to chlorine ratio may be in error by 2 orders of magnitude, at least. Reactions (5) and (7) are explicitly dependent upon pH. The monochloramine to chlorine ratio depends upon pH for pH values less than 7.5 or greater than 9.3. At pH 6.0, the monochloramine to chlorine ratio is 2.1×10^4; and at pH 10.3 it is 6.7×10^4. Outside the pH range of 7.5 to 9.3, the monochloramine to chlorine ratio decreases implying that the chlorine concentration increases. But the data do not reflect an increased extent of reaction. However, as mentioned earlier, the extent of oxidation by chlorine decreased outside the pH range 6.5 to 9.5. It is, therefore, still possible for the chlorine in solution to be the actual oxidizing agent.

Effect of TOC

The kinetics of As(III) oxidation in aged Houston, TX tap water with 1.0 mg/L chlorine dosage are shown in Figure 18. Although the kinetics were appreciably slowed in this water, the reaction reached 95 percent completion as did the oxidation of 100 ppb As(III) in artificial ground water by 1.0 mg/L chlorine. However, the reaction in the aged tap water took 60 minutes to reach completion while the oxidation reaction in artificial ground water reached completion within 5 sec. The oxidation of As(III) in artificial ground water was at least 720 times faster than the reaction in tap water. Presumably the chlorine demand exerted by the 5 mg/L TOC in the aged tap water was responsible for slowing the kinetics of reaction. Hypochlorous acid may undergo the following reactions with organic constituents in water: oxidation reactions, substitution to form either N-chlorinated organics or C-chlorinated organics, or addition reactions. In general, at least part of the chlorine demand of a water is exerted immediately, with other slower reactions occuring at longer chlorine contact times [29]. In fact, the oxidation may be parallel reactions with oxidation by free chlorine occuring immediately, and oxidation by combined chlorine--either chloramines or organic chloramines--occuring at a slower rate for the second stage.

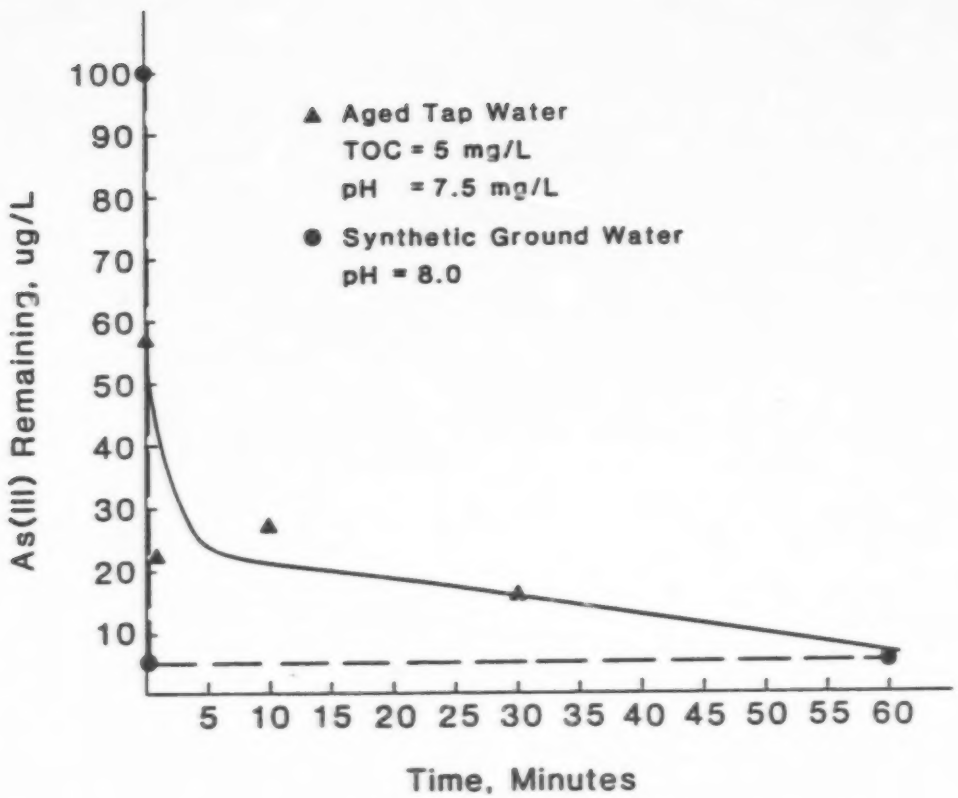

Figure 18. Comparison of the kinetics of oxidation of 100 ppb As(III) by 1.0 mg/L chlorine dosage in aged tap water and artificial ground water.

OXYGEN OXIDANT STUDIES

Sparging Tests

The results of the oxygen sparging tests are presented in Table 13. A sample of 100 ppb As(III) in synthetic ground water, pH 8.3, was bubbled with N_2 at a flow rate of 360 mL/min. Even though glass surfaces reportedly adsorb arsenic [33], ninety seven percent of the arsenic(III) was recovered after the test. In the oxidation tests in artificial ground water, very little, if any, oxidation occurred; whereas, in the DI water, somewhat greater oxidation occurred. Because Cl^- inhibited As(III) oxidation by chlorine, it may also stabilize As(III) with respect to oxygen oxidation; however, effects of the other ions in solution cannot be ignored. The presence of 1.0 mg/L Fe(III) appeared to enhance the oxidation reaction by oxygen slightly.

TABLE 13. The Results of O_2 Oxidation Batch Tests[a]

Conditions	Arsenic(III) Oxidized	
	Synthetic Groundwater[b]	DI Water
pH 6.0	3 %	14 %
pH 7.5	5 %	
pH 8.3	5 %	
1.0 mg/L Fe(II)		16 %
1.0 mg/L Fe(III)	8 % (pH 7.3)	28 % (pH 6)

a) All tests were of 60 minutes duration with 100 ppb As(III) initially.

b) Composition: 2 meq/l Cl^-, 6 meq/L HCO_3^-, 2 meq/L SO_4^{-2}; 1 meq/L Ca, 9 meq/L Na

c) O_2 flow rate = 325-400 mL/min

Despite highly favorable thermodynamic conditions, the oxidation of As(III) appears to occur only very slowly. It is possible, therefore, that the actual oxidizing species is not O_2, but H_2O_2. The mechanism was postulated to account for the very slow kinetics of many oxidation reactions by oxygen. The formation of hydrogen peroxide intermediate is the rate limiting step in this mechanism [37].

As(III) Shelf-Life Experiments

Various standard arsenic solutions were stored in polyethylene bottles and left on a shelf at room temperature and away from direct sunlight. After 61 days, the As(III) fraction was separated at a flow rate of 5 mL/min. The

results of the shelf-life experiments are given in Table 14.

TABLE 14. As(III) REMAINING AFTER 61 DAYS

Initial pH	ppb As(III) Remaining after 61 days		
	DI Water		Synthetic Groundwater
	50 ppb As(III)/ 50 ppb As(V)	200 ppb As(III)	50 ppb As(III)/ 50 ppb As(V)
pH 6.0	0	< 1	
pH 7.0	0	< 1	< 1 (pH 7.3)
pH 8.0	0	< 1	< 1 (pH 8.3)

Note: "0" concentration was indistinguishable from the blank in GFAA analysis for arsenic. "Less than one showed" adsorbance less than 0.007 in GFAA analysis.

These results show that given sufficient time, 61 days in this experiment, air (approximately 21 percent oxygen) is capable of an apparent complete oxidation of As(III) under ambient conditions. These results demonstrate the importance of using freshly prepared As(III) solutions whenever the valence state is important. Adsorption of arsenic onto the polyethylene bottle surfaces was not observed during this experiment. Each solution was analyzed for arsenic immediately after preparation and again at the end of the experiment. All arsenic was still available in solution.

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APPENDIX 1

Equations used for construction of Eh-pH diagram for arsenic and water system:

Dissociation reaction boundaries

$$\frac{[H_2AsO_4^-]}{[H_3AsO_4]} \qquad pH = 2.2$$

$$\frac{[HAsO_4^{2-}]}{[H_2AsO_4^-]} \qquad pH = 6.98$$

$$\frac{[AsO_4^{3-}]}{[HAsO_4^{2-}]} \qquad pH = 11.50$$

$$\frac{[AsO_2^-]}{[HAsO_2]} \qquad pH = 9.22$$

Oxidation-reduction reaction boundaries

$$\frac{[H_3AsO_4]}{[HAsO_2]} \qquad pE = 9.45 - pH$$

$$\frac{[AsO_4^{3-}]}{[AsO_2^-]} \qquad pE = 16.55 - 2\ pH$$

$$\frac{[H_3AsO_4]}{[AsO^+]} \qquad pE = 9.31 - 1.5\ pH$$

$$\frac{[H_2AsO_4^-]}{[HAsO_2]} \qquad pE = 11.27 - 1.5\ pH$$

$$\frac{[HAsO_4^{2-}]}{[HAsO_2]} \qquad pE = 14.91 - 2\ pH$$

$$\frac{[HAsO_4^{2-}]}{[AsO_2^-]} \qquad pE = 10.30 - 1.5\ pH$$

APPENDIX 2

The equations used for the construction of the Eh-pH diagram for chlorine and water are as follows.

Dissociation reaction boundary

$$\frac{[OCl^-]}{[HOCl]} \qquad pH = 7.5$$

Oxidation-reduction reaction boundaries

$$\frac{[HOCl]}{[Cl_2]^{.5}} \qquad pE = 26.9 - pH$$

$$\frac{[Cl_2]^{.5}}{[Cl^-]} \qquad pE = 23.6$$

$$\frac{[HOCl]}{[Cl^-]} \qquad pE = 25.25 - 0.5\ pH$$

$$\frac{[OCl^-]}{[Cl^-]} \qquad pE = 28.9 - pH$$

APPENDIX 3

Chlorine Oxidant Decay Reactions

Breakpoint reaction

$$2\ NHCl_2 + H_2O = N_2 + 3\ H^+ + 3\ Cl^- + HOCl$$

$$4\ HOCl + NH_3 = NO_3^- + 4\ Cl^- + 5\ H^+ + H_2O$$

Oxidation of Carbon

$$CH_2OH(CHOH)_4CHO + HOCl = CH_2OH(CHOH)_4COOC + H^+ + Cl^-$$

$$R\text{-}CHNH_2\text{-}COOH + HOCl = R\text{-}CHO + NH_3 + CO_2 + H^+ + Cl^-$$

Organic Substitution

$$C_6H_5OH + 3\ HOCl = C_6H_2Cl_3OH + 3\ H_2O$$

Disproportionation

$$3\ HOCl = 3\ H^+ + 2\ Cl^- + ClO_3^-$$

Decomposition to Oxygen

$$2\ HOCl = 2\ H^+ + 2\ Cl^- + O_2$$

Inorganic Oxidation

$$NO_2^- + HOCl = NO_3^- + H^+ + Cl^-$$

$$Mn^{2+} + HOCl + H_2O = MnO_2(s) + 3\ H^+ + Cl^-$$

APPENDIX 4

Conditioning Procedure for Activated Alumina

Bed Volume = 50 ml of Alcoa F-1 type alumina, mesh 28 X 48

Rinse	Bed Volumes	
1 % NaOH	10	
DI Water	10	
2 % H_2SO_4	10	
DI Water	10	
1 % NaOH	10	
DI Water	10	
2 % H_2SO_4	10	
DI Water	100	pH = 4.5

Air dried overnight, then dried 24 hr at 105 C

APPENDIX 5

Arsenic Analysis

Step	Temperature	Ramp Time	Hold Time
Dry	110 C	5 sec	25 sec
Char	250 C	5 sec	20 sec
Atomize	2700 C	1 sec	10 sec

Wavelength: 197.7 nm
Gas Flow: Interrupt Argon
Low Slit Width: 0.7 nm

Sample Volume: 20 μL
Matrix Modifier: 20 μL 1000 mg/L $NiNO_3$ as Ni in 2 % HNO_3

APPENDIX 6

Sample	Change in Absorbance	
	Initial Absorbance	Absorbance after 2 minutes
Blank	0	0
1.0 mg/L Cl_2 dosage	0.35	0.45
	0.30	0.38
100 ppb As(III) with 1.0 mg/L Cl_2	0.28	0.40

Background water 0.01 M NaCl